H. A. DuBois Jr.

1927.

A MANUAL

OF THE

DETECTION OF POISONS

BY

MEDICO-CHEMICAL ANALYSIS.

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TRANSLATED FROM THE GERMAN, WITH NOTES AND ADDITIONS,

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THE AUTHOR'S PREFACE.

I HAVE been repeatedly requested by several apothecaries, who have followed with advantage the method for the detection of arsenic in chemiço-legal examinations, as laid down in my "Hand-book of Chemistry," to furnish them with a similar method for the detection of other poisons. In preparing the chapter "On the Detection of Arsenic," for the last edition of my "Hand-book of Chemistry," I resolved to comply with their wishes, and it is thus that this manual of chemico-legal analysis originated; the chapter "On the Detection of Arsenic," is a reprint from the "Hand-book."

All the methods contained in this manual have been tried in my laboratory; they are written down from personal experience and, I think, are deserving of confidence on that account. In the investigations on the detection of the organic poisons, I have had the valuable assistance of Mr. Von Pöllnitz, to whom I beg to express my sincere thanks.

Though this manual is originally designed only for the use of such, who are in the habit of working after a special rule, still, I think, it will not be an unwelcome companion to those who prefer to be led by their own judgment, and who are,

perhaps, able to use better methods in the stead of those given by me; it takes then, at least, the place of a *pro memoriâ*. The manual may also prove useful in chemical laboratories as a guide to the student, and a careful perusal of its contents will undoubtedly be very beneficial to physicians, district-attorneys, lawyers and judges.

In judging of this little work, I beg the reader to bear in mind that it pretends to no more than to be simply a chemical manual.

OTTO.

BRUNSWICK, *January* 1856.

PREFACE OF THE AMERICAN EDITOR.

THE best apology which I am able to offer for having prepared an American edition of Professor Otto's work, lies in the high scientific position of its author, and in its peculiar, systematic arrangement. The numerous works on medical jurisprudence, contain all more or less accurate methods for the detection of the different poisons, but arranged in such a manner that they are only applicable when the nature of the poison is known beforehand; in other words, they contain only methods by which any certain poison may be found, but not a systematic method which will lead to the detection of any poison. Professor Otto has endeavored to bring the whole into a general system, and to establish a mode of procedure resembling that used in qualitative chemical analysis, so that the nature of the poison may be ascertained without any previous knowledge. A short *exposé* of the general method is given p. 171. I have several times had occasion to subject Professor Otto's system to a practical test, and

cannot but acknowledge its superior usefulness. If all the precautions which are mentioned in their proper place, are duly observed, the analyst will certainly obtain very satisfactory results.

The few additions which I have thought proper to introduce, are inclosed in brackets. The more important of these occur in the chapter "On the Detection of Hydrocyanic Acid," which has been extended to about double its original size, and in the chapter "On the Detection of Poisonous Alkaloids," to which I have added the reactions of several alkaloids not mentioned in the German original, and the important physiological tests for strychnine. The chapter "On the Detection of Oxalic Acid," is entirely new.

I have to apologize for the omission of some notes, relating to cases which have come under the observation of the author. While doing so I intended to furnish an appendix, containing a collection of the most famous foreign and all those American cases which offer any interest to the legal chemist; but want of time to bring the necessary material together, and the duties of a laborious professorship, have prevented me from carrying this plan into effect at present.

WM. ELDERHORST.

TROY, New York, *April*, 1857.

ON THE

DETECTION OF POISONS.

CHAPTER I.

ON THE DETECTION OF ARSENIC.

§ 1. ARSENIC belongs to the class of irritant poisons. Of all the members of this group, which embraces the compounds of the metals, it is for the medical jurist the most important. Arsenic and its compounds are more frequently chosen for the purpose of committing both suicide and murder than any other poison. Out of 543 cases of fatal poisoning, brought before the coroners of England, during the years 1837 and 1838, 186 were due to arsenic.—(*Christison.*) In France, 616 accusations for poisoning were brought before the courts, from 1826 to 1845; of these nearly two-thirds were for poisoning with arsenic; for the years 1841 to 1844 the total number of cases was 201; 137 out of which were for poisoning with arsenic.—(*Flandin.*)

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The most usual shape in which this poison is administered is in that of arsenious acid, or white arsenic. But cases of poisoning with fly-powder, with arsenite of copper, arsenite of potassa, arsenic acid, the various sulphides of arsenic, and other compounds are, also, of frequent occurrence. In whatever form the arsenic may have been given, the general analytical process is the same; and it is only in case particles of the poison should be detected unchanged in the stomach or the intestines, that the performance of some special reactions might be required. These are fully described below (§ 4 to 7), for the most frequently occurring compounds.

§ 2. The first thing in beginning a legal analysis is, to convince one's self that the re-agents are perfectly free from arsenic. The barest possibility of this not being the case is sufficient to make a thorough examination, and, if required, purification necessary.*

* The purity of the hydrochloric acid which, in the process for the detection of arsenic and the metals in general, is often used in considerable quantities (several pounds being sometimes required), should more especially be attended to. The acid should be treated with sulphureted hydrogen, for there is no other way to remove those traces of arsenic which are, perhaps, never wanting, but which become only evident in operating on large quantities. Four pounds of crude hydrochloric acid, which I use in my laboratory, for the preparation of pure acid, and which passes generally for being free from arsenic, afforded, on being diluted with an equal volume of water, and treated with sulphureted hydrogen, a deposit in which the presence of arsenic could be distinctly shown by Marsh's test. For the purpose of legal investigations it is very convenient to keep on hand a quantity of acid that has been purified by sulphureted hydrogen; it is sufficiently concentrated.

[Zinc and sulphuric acid frequently contain arsenic, sometimes in

The fact of these operations having been performed should be mentioned in the report (see below).

§ 3. In considering the process followed in the chemical examination, it is most convenient to assume three different cases, as pointed out by *Wöhler:*

I. The arsenious acid is found in the solid state in the contents of the stomach and intestines, or in the vomited matters.

II. The poison is intimately and invisibly mixed with, or dissolved in, the contents, etc., and can, therefore, no longer be found or separated by mechanical means, in the solid state.

III. The stomach and intestines are empty, or no arsenic can be detected in them, since it has already

considerable quantity. Zinc is scarcely ever free of a trace of arsenic, but I never experienced any difficulty in obtaining zinc so pure as to exhibit not a trace of arsenic, by Marsh's method. Jacquelain could not detect an atom in any French specimen of zinc, or its carbonate or silicated oxide, as met with in commerce.—(Journal de Chimie méd. 1842.) Brett satisfied himself that no British or foreign zinc he could obtain indicated the presence of arsenic by a process capable of detecting one 5000th of that metal in zinc. (London Philosophical Journal, 1842.) Schäuffele found in one kilogramme of

French zinc	0.00426	gram arsenic.
Silesian zinc	0.00097	" "
Zinc of Vielle-Montagne . . .	0.00062	" "
Zinc of Corfali	0.00005	" "

(Journ. de Chimie méd. 3 Sér. T. VI).

The amount of arsenic in common sulphuric acid is often very great. Cameron found about an ounce of crystallized arsenious acid deposited, after long standing, from eight pounds of sulphuric acid. (Chem. Gazette, 1856.) The acid sold as pure, in commerce, I found, by my experiments, to be sufficiently free from arsenic to be be used in Marsh's process. In § 18 the method of testing zinc and sulphuric acid for its purity is described.]

been absorbed into the mass of the blood, or into the substance of the different organs.

The most characteristic reactions by which arsenious acid may be recognized, will be given below; and the question, "Is the substance under examination white arsenic?" is easily answered, when the poison is found in the solid state. But, if poisoned food, or contents of the stomach, etc., or vomited matters, blood, urine, or entire organs, ex. gr., liver, spleen, are to be examined, it becomes much more difficult, owing to the presence of organic matter and foreign salts, which cause several of the reactions to become indistinct; and it is for such cases, principally, that the various methods for the detection of arsenic, in legal investigations, are given. In such cases particular attention should be paid to the resemblance of antimony and arsenic, because tartar emetic is frequently administered to produce vomiting when poisoning is suspected.

The famous trial of Madame Lafarge has given occasion to a careful revision, within the last few years, of all the various methods for the detection of arsenic. The result of this revision has led to the conclusion, that the experienced and careful chemist can attain his end by various ways with equal certainty. But it is only the experienced and careful chemist, and no other person, who should be trusted with a legal investigation of this kind; for it is not sufficient that a man knows *how* the thing is done, he should also be able to *do* it, and that on the most approved principles, and with experienced hands. In many cases, the detection of arsenic is a very easy matter; but, if the poison exists in very minute

quantities, it is only with a great deal of care and circumspection that the analyst will be able to prove its presence conclusively. To make the examination as much as possible independent of the individual qualifications and amount of chemical knowledge of the analyst, is the principal object of these pages. They are not intended for the chemist by profession, and to him they are only in so far of value as they contain a compilation of all that has been published on the subject.*

§ 4. White arsenic being but with difficulty soluble,†

* The literary material on this subject is considerable. Among the recent publications the more important ones are the following:

Das forensisch-gerichtliche Verfahren bei einer Arsenikvergiftung, von F. Wöhler und E. v. Siebold. Berlin, 1847; a very excellent pamphlet. Über ein neues Verfahren zur Ausmittelung und quantitativen Bestimmung des Arsens bei Vergiftungsfällen, von Dr. R. Fresenius und Dr. L. v. Babo (Annalen der Chemie und Pharm. Bd 49 p. 287). Das Arsenik, seine Erkennung, etc, von Duflos und Hirsch, Breslau 1842. Hand-book of inorganic analysis, by F. Wöhler; edited by A. W. Hofmann, London 1854; and the treatises on analytical chemistry, by H. Rose, R. Fresenius, etc. A treatise on poisons, by R. Christison, M. D.; American edition, Phil. 1845. Traité des poisons, par Ch. Flandin. Vol. I. Paris 1846. Traité de Toxicologie, par M. Orfila. 5 ed. Paris 1852. Die gerichtliche Chemie, von F. C. Schneider. Wien 1852; and the different works on medical jurisprudence.

[† The solubility of arsenious acid is a point of some medico-legal importance. It is different in the two modifications in which this acid occurs. According to *Guibourt*

100 parts of water contain:	Of the opaque modification.	Of the transparent modification.
Solution saturated at 15° C. . .	1.25	0.96
Solution saturated at 100° C. . .	11.47	9.68
Solution saturated at 100° C. after cooling and resting for 2 days,	2.90	1.78

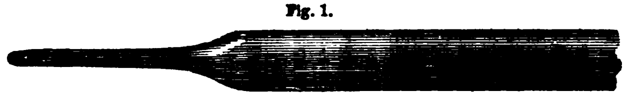
Alfred Taylor observed that water, boiling gently for an hour, dis-

the attention of the analyst ought first to be directed towards finding small fragments of it in the stomach, and especially in those parts which are reddened by inflammation, in the food, the contents, etc. The food, the contents, the vomited matters, etc., are placed in a spacious glass jar, or beaker glass, distilled water poured on it, and the whole well stirred for some time; by this process the grains of arsenious acid are cleaned, and settle to the bottom of the vessel on account of their considerable density. The grains are easily recognized, and carefully picked out with a forceps, after having poured off the supernatant liquid.

To prove that the white grains, thus obtained, really are arsenious acid, the following experiments are made:

A particle of the substance is placed in the lower

Fig. 1.



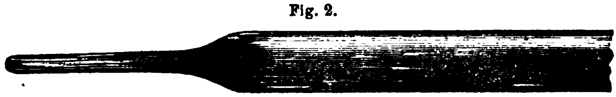
and very narrow part of a glass tube, of the shape

solved 3.15 per cent. of the opaque modification, and, on cooling and resting for 3 days, retained 1.7; that, with violent ebullition for an hour, it took up 4.63, and retained 2.47 on cooling and resting for 3 days; and that a saturated boiling solution of the transparent modifications contained 4.6 or 4.75 per cent., and on cooling and resting for 2 days retained 1.87 or 1.34.

The presence of organic principles appears to impair its solubility Christison found that a cup of tea, left beside the fire at a temperature of 200° F. for half an hour upon 2 grains of the acid, does not entirely take up even that small quantity. These observations account for the fact, that frequently little or no arsenic is found in the fluid contents of the stomach, after an exhibition of the poison in the solid state.]

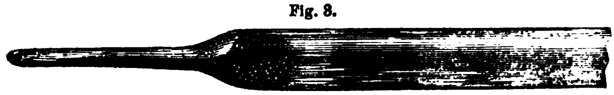
shown in Fig. 1; immediately above, and also in the narrow part of the tube, is placed a thin splinter of freshly ignited charcoal. This part of the tube is now held horizontally in the very small flame of a common spirit lamp, in such a manner that the spot where the arsenious acid is placed may remain beyond the flame. When the charcoal is heated to redness, the open end of the tube is raised higher and higher, so that the tube becomes more and more inclined, until the spot where the arsenious acid is placed is also touched by the flame. If the particle was arsenious acid, it vaporizes; the vapor on its passage over the red hot charcoal is decomposed, and metallic arsenic is deposited beyond the charcoal, in the form of a black, or brownish-black, lustrous ring (arsenic mirror), as is illustrated by Fig. 2.

Fig. 2.



By applying heat, this incrustation of metallic arsenic vaporizes, becomes oxidized, and condenses in the wider part of the tube to a sublimate of arsenious acid, consisting of minute, lustrous crystals which, when seen with a lens or a microscope, appear as distinct octahedrons. The tube presents the appearance as shown in Fig. 3.

Fig. 3.



If the narrow part of the tube below the arsenic mirror is cut off, and the spot where the incrustation

is situated heated, by holding this end of the tube, slightly inclined upwards, into a small alcohol flame, a bluish white coloration of the flame will be observed where the arsenic vapor enters the flame, and the characteristic alliaceous odor is distinctly perceived on quickly approaching the tube to the nose.

The successful process of reduction, the odor of the vaporized arsenic mirror, and its conversion into a white crystalline sublimate, are sufficient proofs that the white substance under trial consists of arsenious acid.

§ 5. If several grains of arsenious acid have been collected, another experiment of reduction should be made, and the tube with the mirror handed over, together with the written report, to the proper authorities, as a *corpus delicti;* the remaining grains are used for other experiments:

A particle is introduced into a glass tube sealed at one end, some dry acetate of soda, or potassa, added, and heat applied, when the indescribably offensive and characteristic odor of alkarsin (oxide of kakodyl) should be evolved.

One or more fragments are finely powdered in a small agate mortar, the powder dissolved in boiling water, and the solution mixed with a few drops of a solution of nitrate of silver; some very dilute caustic ammonia is then added, drop by drop, or by means of a glass rod, when the characteristic yellow precipitate of arsenite of silver will be produced.

The watery solution is acidulated with a few drops of hydrochloric acid, and some freshly prepared and strong sulphureted hydrogen water

added, when a yellow precipitate of sulphuret of arsenic should be produced.

A fragment is heated in a test-tube with some nitric acid, to form arsenic acid; a few drops of nitrate of silver, and, afterwards, dilute ammonia, drop by drop, are added, when the reddish brown precipitate of arsenate of silver should be produced.

A fragment is converted into arsenic acid, as before, and the solution over-saturated with ammonia; a solution of chloride of ammonium, and, afterwards, a solution of sulphate of magnesia is added, when a crystalline precipitate of arsenate of magnesia-ammonia is thrown down, if the substance under examination was arsenious acid.

A fragment is used to form arseneted hydrogen, after the manner explained below.

§ 6. In examining the matter under examination for the presence of solid arsenious acid, proper regard should at the same time be paid to the presence of metallic arsenic, since the latter, known also under the name of "fly powder," is as easily accessible to the public as white arsenic; it also possesses poisonous properties, and may, and indeed has been, employed for the purpose of poisoning; it always contains some arsenious acid.

The fly powder is found in the shape of small black, or brownish black, lustrous, heavy scales or grains, the nature of which is as readily ascertained as that of arsenious acid. Heated in a glass tube (Fig. 1) alone, it yields an arsenic mirror. Thrown on incandescent charcoal, it evolves the characteristic alliaceous odor.—The powder, when heated with nitric acid, yields, with evolution of nitrous acid

vapor, a solution of arsenic acid (or of arsenious acid if the heat was not kept up for a sufficiently long time, or not sufficient nitric acid added); the liquid is carefully neutralized with ammonia, and then a few drops of nitrate of silver added, a reddish brown (eventually a yellow) precipitate is produced; after oversaturation with ammonia, a solution of sulphate of magnesia, containing chloride of ammonium, produces a white crystalline precipitate of arsenate of magnesia-ammonia; and an addition of sulphureted hydrogen water produces, immediately or after some time, and especially on gently heating, a yellow precipitate of sulphuret of arsenic.

[§ 7. If a sulphide of arsenic has been administered, the examination of the contents of the stomach and intestines may yield some fragments of this substance. The bisulphide of arsenic, or *realgar*, is of a bright red, or orange yellow color, resinous lustre, and very brittle. The tersulphide, or *orpiment*, is a golden yellow crystalline substance. Both are volatile; heated in a glass tube closed at one end, they afford sublimates of different color; sometimes three sublimates are produced, the most volatile one being of a yellow, the next of a red, and the least volatile of a black color. They are insoluble in water, only slightly affected by acids, but soluble in ammonia; on adding an acid to the ammoniacal solution, the sulphide is re-precipitated. Their nature is most satisfactorily and indubitably ascertained by subjecting a fragment to the treatment described in § 13, and testing the resulting liquid after Marsh's method.

Fragments of *Scheele's green* (arsenite of copper), or other arsenites which may have been found in the

stomach, are most conveniently treated with a mixture of cyanide of potassium and carbonate of soda, as described in § 25.]

§ 8. If arsenious acid or fly-powder cannot be found in the solid state, the mass (the contents of the stomach and intestines, and even these organs themselves, the food, the vomited matters, etc.) must be subjected to a further treatment; but, even if particles of arsenious acid or fly-powder have been found, it is, in most cases, advisable, or even necessary, to extend the investigation for the presence of arsenic in these substances still farther, if it were only to form an opinion as to the amount of the poison. With reference to the course of action to be pursued, we may remark here, that the food, the contents, the vomited matters, etc., have, each of them, to be treated separately. The separation of the contents of the intestines from those of the stomach may be of special interest in deciding the question, whether arsenic has passed from the stomach into the intestines.

It is furthermore advisable to set a portion of the mass aside, and to reserve it, so that in case of an accident the analyst may be enabled to begin the examination anew. It may be said, without hesitation, that where there is arsenic undoubtedly present, half of the mass will be sufficient to detect it with certainty, at least in 99 cases out of 100. Before dividing the mass for this purpose it should be uniformly mixed.

§ 9. The first operation consists in destroying the whole of the organic matter and dissolving the whole of the arsenic.

The mass under examination is (after having been

cut into shreds, if necessary), introduced into a porcelain dish, and about as much pure concentrated hydrochloric acid added as is equal to the weight of the dry substance contained in the mass, or a little more, and enough water to form the whole into a thin paste. If the substance has previously been mixed and stirred with water, as mentioned above, for the purpose of detecting particles of solid arsenious acid, it may be necessary to remove part of the water by evaporation in the water-bath, before adding the hydrochloric acid; this however, will be but rarely required. The dish is then placed into a water-bath, or steam-bath, and to the hot mass some pure chlorate of potassa added, at intervals of five minutes, in portions of about half a drachm each (2 grammes), until the whole is converted into a perfectly homogeneous, light yellow, liquid mass. When this point is reached, another addition of about 2 drachms (8 grammes) of chlorate of potassa is made, and the heat continued until the smell of chlorine has entirely disappeared. If the liquid should become too concentrated by evaporation, a little water is from time to time added. The mass is now allowed to cool; the contents of the dish are thrown on a moistened filter of white paper, free from smalt; when the quantities are large, a white linen cloth may be substituted, and the residue washed with hot water. The washings are collected in a separate vessel; if they yield too much liquid, they are evaporated on a water-bath in a porcelain dish, and, after having been sufficiently concentrated, united with the first filtrate. The whole of the liquid should amount to about a pint.

The chemist will readily understand the object of this operation. The chlorine, or the compounds of chlorine, which are formed and set free by the action of the hydrochloric acid on the chlorate of potassa, act decomposing on the organic substances, and convert the arsenic, in whatever form it may occur, even when present as sulphuret, in arsenic acid.

In consideration of the fact that, from a liquid containing arsenious or arsenic acid, and hydrochloric acid, chloride of arsenic may escape in the gaseous state, the analyst might feel inclined to perform the operation, viz.: the treatment of the mass with hydrochloric acid and chlorate of potassa, in a tubulated retort, connected with a receiver. In regard to this, experience has shown that, at the temperature to which the mass is raised, when heated in a water, or vapor-bath, no perceptible quantity of arsenic is lost, but that an evaporation of the concentrated liquid is not admissible. There is, however, no objection to using a retort. The retort is placed on a wire-gauze over the furnace, and a moderate heat applied. The distillate must be examined separately. If it is deemed necessary to concentrate the liquid by evaporation, it has to be done in a retort, the temperature being kept below the boiling point.

§ 10. The next operation is the precipitation of the arsenic from the liquid as sulphide. The liquid is poured into a spacious beaker-glass, or a flask, and a current of washed sulphureted hydrogen gas slowly passed through it; when the liquid is perfectly saturated with gas, it is heated to about 140°–170° F., which is done by placing the vessel containing it into hot water; it is then allowed to cool, the gas all the while

passing through it, and finally set aside, well covered, at a moderately warm place, for about twenty-four hours. If, after this time, the odor of sulphureted hydrogen should be but faint, sulphureted hydrogen gas is again passed into it, and the liquid again left standing for some time, at a moderately warm place. By this means, and only by this means, viz.: by a continued and repeated treatment with sulphureted hydrogen, the whole of the arsenic is removed and precipitated as sulphide.

With regard to this operation, it must be borne in mind that arsenic acid, and in this state the arsenic is contained in the liquid, is but slowly decomposed by sulphureted hydrogen. Heat aids and facilitates the decomposition of the acid and the precipitation of the sulphide.

The precipitate contains, besides sulphide of arsenic, organic matter and, if lead, copper, mercury, and antimony were present in the liquid, the sulphides of these metals. The color of the precipitate is, in this respect, suggestive.

If there is only a very minute quantity of arsenic present, it may happen that, after the treatment with sulphureted hydrogen, in the above indicated manner, not the slightest trace of a precipitate is deposited. It then forms on evaporation, in the measure as the acid becomes more concentrated; and hence, in a case like this, it should never be omitted to evaporate the liquid, and to treat the concentrated liquid repeatedly with sulphureted hydrogen gas.

On the other hand, the formation of a precipitate, after the passage of a current of sulphureted hydrogen gas, does not warrant the inference that arsenic

is present, since, almost invariably, a deposition of organic matter, even in absence of arsenic, takes place. If sulphureted hydrogen is passed into the liquid, which is filtered off from the first precipitate, caused by sulphureted hydrogen, another precipitate will be formed, even if it no longer contains any arsenic.

Since arsenious acid is much more readily, and within a much shorter time, decomposed by sulphureted hydrogen than arsenic acid, it has been proposed to reduce the arsenic acid, contained in the liquid which results from the treatment of the original substance with hydrochloric acid and chlorate of potassa, by means of sulphurous acid to arsenious acid before passing sulphureted hydrogen into it. For this purpose, the liquid is heated in a water-bath, and so much of a concentrated solution of sulphurous acid, or sulphite of soda added that the odor of sulphurous acid is distinctly observable; the heat is then continued until the odor has entirely disappeared. Woehler himself, with whom the proposition originated, afterwards abandoned the use of sulphurous acid.

§ 11. The next operation consists in collecting and purifying the precipitate. After the liquid, still highly charged with sulphureted hydrogen, has cooled, the precipitate is transferred to a small filter, and well washed, at first with water containing some sulphureted hydrogen.* To remove other me-

* Formerly it was laid down as a rule to set the liquid aside before filtering it, until the whole of the sulphureted hydrogen had evaporated, and the principal object of placing the vessel at a moderetely warm spot, was to facilitate the escape of the gas. But it has

tals which might be mixed with the sulphide of arsenic, the precipitate is most advantageously treated with dilute ammonia. For this purpose, the filter containing the moist precipitate is spread out in a porcelain dish, and a little water poured on it; the precipitate is then divided into a thin, homogeneous paste, by means of a feather, and ammonia added, drop by drop, as long as solution takes place, or until an excess of the solvent is clearly indicated by the odor. Sulphide of arsenic and the organic substances dissolve in dilute ammonia, and the other metallic sulphides, which might have been precipitated by the sulphureted hydrogen, remain undissolved; only a small quantity of sulphide of antimony might, also, enter into solution. The ammoniacal liquid, which is of a dark-brown color, is strained through a small filter, and the residue carefully washed with ammoniacal water. This residue has to be examined for antimony, lead, copper, mercury, etc.

The treatment of the precipitate with dilute ammonia may, also, be thus executed: dilute ammonia is poured, drop by drop, on the filter containing the moist precipitate, while still in the funnel, care being taken, if the precipitate is of a slimy and viscous consistency—as is almost invariably the case when organic matter is present—to bring it into contact with the liquid by stirring it with a feather; or the dilute ammonia is applied by means of a washing-bottle.

Instead of the dilute liquid ammonia, a saturated solution of carbonate of ammonia may be employed

been shown by Becker, that the precipitated sulphide of arsenic becomes sensibly oxydized, after the whole of the sulphureted hydrogen has passed off.—(Archiv der Pharm. Vol. 56, p. 287.)

for the purpose of extracting the sulphide of arsenic from the precipitate; the latter reagent acts less solving on sulphide of antimony, which might be present, but acts, also, less energetic on the sulphide of arsenic.

The ammoniacal solution, together with the washings, is then placed in a porcelain capsule, and evaporated to dryness at a gentle heat; the sulphide of arsenic, if present in the precipitate, remains, mixed with the organic matter, as a dark-brown residue.

§ 12. The only conclusive proof of the presence of arsenic in this residue, and, consequently, in the substances under examination, is its separation in the metallic state, its reduction to metallic arsenic. To effect this reduction, the sulphide or the acids of arsenic, prepared from the sulphide by oxidation, may be employed. But, even if the reduction is to be made directly from the sulphide, after the manner hereafter to be described, it is not admissible to use the residue itself without any further preparation, since the products of the destruction of the organic matter may cause the reaction to become quite indistinct. The organic substances, contained in the residue, must, therefore, first be destroyed, either by nitric acid and fusion with nitrate of soda, or by nitric acid and sulphuric acid; we then obtain a mass, containing arsenic acid, which may be used directly for the process of reduction, or from which pure sulphide of arsenic may be prepared.

§ 13. The safest method to effect the destruction of the organic matter, and the oxidation of the sulphide of arsenic, is fusion with nitrate of soda. Some highly

concentrated or, better still, fuming nitric acid is poured on the residue, in the porcelain capsule, and the acid evaporated at a gentle heat. If the residue which is now left is still of a dark color, this treatment with nitric acid has to be repeated, until the residue, while moist, appears of a yellow color. To the residue some caustic soda is now added, which serves to neutralize the excess of acid without effervescence and to soften the mass, and, afterwards, some finely powdered carbonate of soda, and some nitrate of soda, also finely powdered, and the whole placed in a porcelain crucible. The capsule is cleaned out with a little carbonate of soda, which is then added to the mass in the crucible. The contents of the crucible are now thoroughly dried, and then heated by means of a spirit-lamp, care being taken that the temperature rises very gradually. At first the mass turns brown, or black, becomes afterwards decolorized, without deflagration, and, finally, fuses to a colorless liquid. The whole of the organic matter is then completely destroyed.

The fused mass contains, if arsenic was present, arsenate of soda, besides nitrate, nitrite, sulphate, and carbonate of soda; and, in case the precipitate contained antimony, antimonate of soda. The mass is treated with water; if antimonate of soda was present, this remains undissolved, and is separated by filtration; the liquid is strongly acidulated with dilute sulphuric acid, precaution being taken that no loss is incurred by spirting, and evaporated in a porcelain capsule. Towards the end of the operation some more sulphuric acid is added, to make sure of its being present in sufficient quantity to expel the whole

of the nitric and nitrous acids; the only safe indication for this is the appearance of the thick sulphuric acid vapors, and the evaporation must be continued until this takes place.—(Meyer, Annalen der Chemie und Pharmacie, Bd. 66. p. 237.) The elimination of the antimony, and the complete destruction of the organic substances, greatly recommends this treatment of the crude sulphide of arsenic. To prevent volatilization of the arsenic as chloride of arsenic, it is requisite that all materials, viz.: the nitric acid, the caustic soda, the carbonate and nitrate of soda, be perfectly free from chlorine.

The mass obtained by evaporation, usually a colorless and very acid liquid, is very well adapted for the preparation of metallic arsenic by the process of Marsh (see below).

If the preparation of sulphide of arsenic is intended, for the purpose of subsequent reduction by another process, the mass is most conveniently treated with a concentrated solution of sulphurous acid; the excess of this acid removed by heat, and a current of sulphureted hydrogen passed through the moderately hot liquid, until the whole of the arsenic is precipitated. The sulphide is collected on a small filter, well washed, and, finally, dissolved in dilute ammonia by pouring the solvent, drop by drop, on the filter, as above described. The solution, on evaporation in a porcelain dish, yields the pure sulphide.

§ 14. Fresenius recommends to effect the destruction of the organic matter of the residue in question—the residue from the evaporation of the ammoniacal solution of the crude sulphide of arsenic (§ 11)—by means of nitric acid and concentrated sulphuric acid.

The residue is mixed with some fuming nitric acid, and heated, over a water-bath, to dryness; this residue is moistened with some pure concentrated and heated sulphuric acid, placed upon the water-bath for about two or three hours, and then exposed to a higher temperature (above 150° C.), until it is converted into a charred mass; this mass is treated with from ten to twenty parts of distilled water, filtered and washed. The liquid, thus obtained, is well adapted for Marsh's test; but when used for the purpose of precipitating the arsenic as sulphide, the latter is not, or at least not always, obtained perfectly free from organic matter.

§ 15. Instead of treating the precipitate (§ 10), obtained from the solution of the substance under examination by means of sulphureted hydrogen, with dilute ammonia, to evaporate the solution and heat the residue with nitric acid, etc., as mentioned in the preceding paragraph, it has been recommended to treat the precipitate, together with the filter, directly with nitric acid, etc. But since it is so easy a matter to exclude the paper of the filter, why not do it? And since it is always advisable to test for the presence of other sulphides, insoluble in ammonia, why then omit the treatment with ammonia?

§ 16. We will now take into consideration the reduction of the arsenic, which, as above (§ 12) stated, is the only conclusive proof for the presence of the poison, partly because the arsenic, in its metallic state, is easily recognized as such, and partly because the process of reduction can be executed in such a manner as to exclude the possibility of its being

confounded with any other metal. Of the various methods of reduction which have been proposed, only two deserve our attention, viz., the process of Marsh, or rather the improved method developed on the base of Marsh's original process, and the process of Fresenius and Babo. The process of Marsh is more simple and more easily executed than that of Fresenius and Babo, it requires less experienced and less cautious hands for its execution, it yields very various and characteristic proofs for the presence of the metal, and admits of an easy application of the various reagents for examining the nature of the metallic mirrors. But the process of Fresenius and Babo surpasses that of Marsh in this respect, that it excludes the possibility of confounding arsenic with antimony. The process of Marsh does not yield the whole of the arsenic, as we shall see hereafter, whereas the process of Fresenius and Babo affords the whole of it in the reduced state, but it is scarcely possible to entirely prevent the escape of a part of the metal. In this respect, therefore, the two methods may be considered equally good. According to my observations, the process of Marsh produces more distinct and characteristic evidence of the presence of very small quantities of arsenic than that of Fresenius and Babo. In the great majority of cases of poisoning, however, there will be sufficient material to employ both processes.

§ 17. We will first direct our attention to the process of Marsh. It is founded on the observation that hydrogen and arsenic, when meeting in the moment of being set free from combination, that is, when in the nascent state, unite to arseneted hydrogen, from

which the arsenic may be obtained in different manners, *ex. gr.*, by heat or by incomplete combustion; and which, on being passed through solutions of salts of easily reducible metallic oxides, yields its arsenic as arsenious acid. The different kinds of apparatus which have been proposed for the execution of the operation may all be replaced by the simple arrangement represented in Fig. 4.

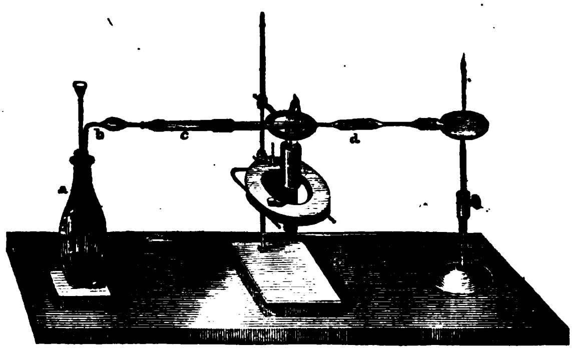


Fig. 4.

It consists of a gas-bottle (a), which may be substituted by a small Woulff's bottle or any other two-necked bottle, provided with a funnel-tube, another tube (b) bent at a right angle, a small drying-tube (c), and a reduction tube (d).

The bulb of the tube (b) serves to condense and collect the greater part of the particles of liquid which are carried off mechanically, or by evaporation, from the contents of the bottle. When a Woulff's or a two-necked bottle is used as gas-generating vessel, the bulb is more conveniently situated on the descending leg of the tube. The descending leg must be suffi-

ciently large in diameter, and cut obliquely at the end, to facilitate the dropping back of the condensed liquid into the bottle.

The drying-tube (c) contains some fused chloride of calcium, and sometimes a small piece of caustic potassa;* some loose cotton, introduced at both ends of the tube, prevents the pieces from falling out. According to my experience, the reduction-tube (d), made of glass, free from lead, is most conveniently one centimetre in diameter, the thickness of the glass being one and a half millimetres, and seven millimetres the diameter of the bore. Fig. 5 represents a section in natural size. The tube is narrowly drawn out in several places, as shown in Fig. 4, and there the arsenic is made to condense by heating the wider part of the tube immediately preceding.

Fig. 5.

If the tube is of the above-mentioned thickness the heating may be effected by means of an alcohol-lamp with Argand's burner, without causing the tube to bend, provided the ignited portion of the tube to rest on the ring of the lamp, and the bent part to be supported. This is very important; for there is nothing more disagreeable and annoying

* In consequence of recent experiments I must insist on having the tube filled with hydrate of potassa alone, or hydrate of potassa in the first half of the tube, and chloride of calcium in the last. This is necessary, because every atom of sulphuric acid which is carried from the gas-bottle into the tube containing the chloride of calcium, sets some hydrochloric acid free, which, by its presence, prevents the formation of the arsenic-mirror. This precaution is absolutely necessary when a liquid containing hydrochloric acid is introduced into the gas-bottle.

than to be obliged to guard during the performance of the experiment against the softening and collapsing of the tube. The opening of the narrowly drawn out ascending leg of the tube must neither be too wide nor too narrow.

The mode of connecting the different tubes with each other depends, of course, upon their respective diameters. The most simple way is to take the drying-tube of the diameter of the reduction-tube, and to draw it out at the other end to the diameter of the delivery-tube (b). Two small tubes of vulcanized India-rubber are then sufficient to effect a close connexion; they fit so well that an additional tying is quite superfluous. The India-rubber tubes, though fitting tightly, still are movable on the glass-tube, and thus admit of the ascending leg of the reduction-tube being turned downwards.

§ 18. We now proceed to the process of reduction. Some pure zinc, granulated or in bars, and in not too small a quantity (several ounces), is introduced into the bottle; connection is then made between the different parts of the apparatus, and so much water poured through the funnel-tube, that its lower end dips into the liquid; some pure distilled sulphuric acid, previously mixed with three parts of water, is then added in small portions to produce a moderate evolution of hydrogen. If the mixture of sulphuric acid and water is applied after perfect cooling, and only small portions at a time are added, the temperature of the bottle (a) will be but slightly raised—and this is of great importance, since under such circumstances only a gas is obtained which is not charged with too much watery vapor.

When all the atmospheric air may be supposed to have been expelled from the apparatus, the escaping gas is kindled, and the flame made to strike against a dish or a saucer of glazed white porcelain, which is held horizontally into the flame. If black spots, or only traces of black spots are deposited on the porcelain, the materials, the zinc or the sulphuric acid, are not free from arsenic, and are not fit to be used; even the apparatus has become useless, or, at least, requires to be very carefully cleaned. The corks must, at all events, be replaced by new ones.

If no spots, or traces of spots, are deposited on the porcelain, we cannot yet rest convinced of the purity of the materials, but must proceed to a second and more stringent examination. This is done by heating the reduction-tube before the first narrowing to redness, by means of a spirit-lamp with Argand's burner, and allowing the gas to pass through for at least half an hour, an equal evolution of hydrogen being sustained by occasional additions of acid. If after this time not the slightest trace of a metallic mirror or coating is deposited in the tube beyond the heated portion, which is tested by holding the tube against a sheet of white paper, the materials may be used for our purposes, for they are either free from arsenic, or contain a quantity not sufficient to interfere with the results. But if a mirror or crust has been formed, purer materials must be looked for. It is a great advantage of the process of Marsh, that it admits of this easy mode of testing the purity of the necessary materials, and in the very same way that is followed to detect the presence of arsenic.

§ 19. After the purity of the materials has thus

been established, we may now proceed with the process of reduction proper. If, for the purpose of the examination of the materials, only a provisional reduction-tube has been used, it is now exchanged for another provided with more narrows, and if the contents of the drying-tube should have become too moist, this is also exchanged for another which lies ready prepared and connected by India-rubber with the new reduction-tube; the whole takes but a few moments. It may, possibly, also be necessary to replace the zinc, or, at least, to pour off the liquid, which may have become too much saturated by sulphate of zinc.* It is hardly necessary to mention that if a replacement of any parts of the apparatus has taken place, or the bottle itself has been opened, care must be taken to drive out all atmospheric air from the apparatus by a sufficiently long-continued evolution of gas before proceeding any further.

While the reduction-tube is in a state of vivid incandescence at the part immediately before the first narrowing and the escaping gas burning, the liquid to be tested for arsenic is poured into the bottle through the funnel-tube, and washed down with a little water. This liquid is either the one mentioned (§13), prepared by treating the precipitate obtained by sulphureted hydrogen with nitric acid, fusion with nitrate and carbonate of soda, etc., or the one men-

* If a three-necked Woulff's bottle has been used, and the middle neck been provided with a cork, through which a syphon-tube has been tightly fitted, the liquid may be removed through the syphon by closing the opening of the reduction-tube with the finger, or better by compressing one of the India-rubber connection-tubes.

tioned (§14), prepared by treating the same precipitate with nitric and sulphuric acid; in both the arsenic, if present, is contained as arsenious or arsenic acid.

If the liquids under consideration contain arsenic, the escaping hydrogen gas becomes mixed with arseneted hydrogen, and in passing through the ignited part the latter is decomposed, and immediately beyond this place, at the narrow portion of the tube, a mirror or coating of arsenic is deposited.

Having thus obtained a mirror or a distinct coating, the flame of the lamp is made smaller, so that the tube remains no longer incandescent. In consequence of this the flame of the escaping gas immediately assumes a bluish-white color, and the above-mentioned spots are formed on porcelain when this is held into the flame; of these spots a sufficient number is prepared to serve as material for further experiments.

It is desirable to obtain, at least, a second metallic mirror in the reduction-tube; but after that the tube is turned in such a manner that its originally ascending leg hangs downward; the flame of the escaping gas being extinguished it is inserted into a test-tube, or a small beaker-glass, partly filled with a solution of nitrate of silver. On then diminishing the heat, and thereby preventing the decomposition of the arseneted hydrogen, this gas passes through the solution of the nitrate of silver, by which it is completely decomposed. The solution blackens in consequence of the elimination of metallic silver, and the liquid contains arsenic in the state of arse-

nious acid, together with the excess of the silver-salt. To prevent the latter from becoming too considerable, it is advisable to take at first a dilute solution, acidulated with a drop or two of nitric acid, and adding gradually of a more concentrated one, in case a large deposit of metallic silver should be formed. In this experiment the reduction-tube may be substituted by a common delivery-tube, bent at a right angle.

§ 20. Simple as the above-described experiments are, their execution, if they shall lead to reliable results, requires the careful observance of some precautions. The following remarks contain all that can be said about them:

The liquid to be tested for arsenic should not be poured into the bottle at once, but at first only a part of it, and the effect be well observed. If the liquid contains arsenic the evolution of gas will increase considerably after its addition, owing to the precipitated arsenic forming a galvanic pair with the zinc; the pure zinc then dissolves as rapidly in the acid as impure zinc. Suppose now a very large quantity to have been added, the evolution of gas may, for this reason, and also because the amount of acid is increased, become very violent, and the operator would be obliged to allay it by pouring cold water into the apparatus, or by surrounding the bottle with cold water. It is, on this account, also advisable not to add the liquid in question until the evolution of gas is more moderate.

If the reduction-tube is sufficiently heated, if the evolution of gas is not too rapid, and if the escaping gas does not contain a large amount of arseneted

hydrogen, the whole of the arsenic is deposited, the whole of the arseneted hydrogen becomes decomposed, and no appreciable quantity of the reduced arsenic is mechanically carried away by the current. But if the reverse is the case, the flame of the burning gas becomes colored, and spots may be obtained on porcelain during the process of reduction.

Spots on porcelain are very readily obtained if the amount of arseneted hydrogen is large, but it requires some nicety of management if only traces of this gas are present.

The opening of the tube must not be too narrow; the current of gas must not be too strong —the gas must not escape with violence, the flame must not be pointed—and the porcelain must be held horizontally and close to the opening of the tube. According to my experience, it is best to cause the spots to be deposited on the inner surface of small porcelain dishes, which must be new, or at least very white and clean; it is convenient to collect the spots on different dishes, so as not to be obliged to make the tests of the subsequent examination of them in one and the same dish. Instead of dishes, small saucers may be used, provided the porcelain be genuine; delf with a lead-glazing is quite inadmissible. The temperature of the dishes should be that of the surrounding air; if they are held into the flame while too cold, water is deposited, and the arsenic floats as a brown coating on the drop. On the other hand, a spot of the dish must not be held into the flame for any great length of time; otherwise, the place becomes so hot that a deposition of arsenic can no

longer take place, and sometimes the arsenic-spot even disappears.

§ 21. It is, as above indicated, one of the great advantages of this apparatus, that it furnishes different and equally characteristic proofs for the presence of arsenic. The principal object ought to be, to obtain one or several depositions of metal in the reduction-tube. If these not merely appear as transparent coatings, but as real metallic mirrors, then there is sufficient arseneted hydrogen mixed with the escaping gas to produce spots on porcelain, which, in this case, should be collected at the same time. When a sufficient number of spots has been obtained, the gas is passed, for a length of time, through the solution of nitrate of silver, and thus the loss of any recoverable arsenic prevented.

In this process, as originally described by Marsh, attention was only paid to the formation of the spots on porcelain; and it was Berzelius, if I mistake not, who first noticed the deposition of metallic arsenic from the gas by heating: an observation which has, afterwards, become of the highest importance.

§ 22. It is only the acids of arsenic, and the solutions of the arsenites and arsenates of potassa, soda, lime, and similar bases, when acidulated with sulphuric acid, and chloride of arsenic, which cause the formation of arseneted hydrogen; neither sulphide of arsenic nor metallic arsenic produce the slightest trace of this gas. The first-mentioned compounds even do not give rise to the formation of this gaseous compound, unconditionally; the absence of certain substances is required. Free chlorine, nitric acid,

and similar oxidizing bodies, moreover the salts of mercury and, probably, some other metallic salts entirely prevent its generation. It is, for this reason, advisable to prepare the liquid to be introduced into the apparatus, exactly as above described; we have then only to guard against the presence of nitric acid. Hydrochloric acid does not influence the formation of arseneted hydrogen, but, since this acid is very volatile, it is better to exclude it, especially because, according to Wackenroder, it sometimes gives rise to the production of spots in absence of arsenic (zinc spots).

§ 23. The liquid which Marsh originally recommended as fit to be introduced into the apparatus, was prepared by simply extracting the organic matters with dilute hydrochloric or sulphuric acid, and, if necessary, concentrating by evaporation. But against the applicability of this liquid serious objections may be raised; the extract may contain substances which may prevent the evolution of the arseneted hydrogen; during the evaporation, chloride of arsenic may be volatilized; the organic matters contained in the liquid usually produce a considerable intumescence, whereby the contents of the bottle are caused to enter the tubes, and thus thwart the experiment. The method of allaying the intumescence by pouring oil, or alcohol, on the liquid, as has been proposed, cannot be relied on; and since, moreover, experience has shown that hydrogen gas, evolved from liquids which contain organic matters, is capable of producing brown spots on porcelain, the direct application of the extract under consideration is usually inadmissible. Nor can we, for the reasons

above stated, recommend the use of the liquid which is prepared by treating the substances with hydrochloric acid and chlorate of potassa.

§ 24. If the precipitate which is thrown down by sulphureted hydrogen is treated with a dilute solution of caustic potassa, the sulphide of arsenic, if present, enters into solution, and, on boiling the liquid with protoxide of copper, sulphide of copper and arsenate of potassa are formed. The liquid, after having been acidulated with sulphuric acid, is well adapted for Marsh's apparatus, but offers no advantages over the solution prepared after our method.

If, in the substances under examination, solid arsenious acid has been detected, and it is thought desirable to subject it to Marsh's test, it is only necessary to dissolve it in pure water, or water acidulated with sulphuric acid, and to pour this solution into the gas-bottle.

§ 25. A short time after the publication of the process of Marsh, Pfaff and Thompson made, independently of each other, the interesting discovery that there exists an antimoneted hydrogen, formed under the same circumstances as arseneted hydrogen, and exhibiting the same phenomena on being heated, burnt, etc. Thus, for example, if we add to the zinc and dilute sulphuric acid of our apparatus some oxide of antimony, or chloride of antimony, or tartar emetic, the escaping hydrogen becomes mixed with antimoneted hydrogen; the flame of the burning gas appears white, spots of metallic antimony are deposited on porcelain which is held into the flame, a mirror of metallic antimony is formed within the ignited tube, and, if the gas is allowed to pass

through a solution of nitrate of silver, a black precipitate is thrown down. Quite the behavior of arsenic!

This discovery of Pfaff and Thompson caused the test of Marsh to be considered very fallacious; the more so, as in a case of suspected poisoning tartar emetic is frequently administered as an emetic. The whole process, therefore, ought to be condemned, unless means are found either wholly to exclude the antimony, or to show, with certainty, that the reactions are produced by arsenic.

If the precipitate thrown down by sulphureted hydrogen (§ 10), is treated directly with nitric acid, and the residue with sulphuric acid, the resulting liquid will, of course, contain all the antimony which might have occurred in the substances. But if the treatment with nitric acid is preceded by a treatment with dilute ammonia, or with a solution of carbonate of ammonia, the antimony is almost wholly, even to a trace, excluded; and if, moreover, the residue resulting from the evaporation of the ammoniacal solution is not treated with nitric and sulphuric acid, but oxidized with nitric acid, and afterwards fused with nitrate and carbonate of soda, the filtered watery solution of the fused mass contains no antimony, this metal remaining behind after the treatment with water as insoluble antimonate of soda (§ 13).

But, even if all these precautions, which effectually exclude the presence of antimony, have been observed, it is necessary to prove the reactions obtained by the process of Marsh to be owing to arsenic, and

it will be the duty of the judge to ask for these proofs. A vast number of characteristic tests for the discrimination of arsenic from antimony have been advanced, in the course of time, so that it is almost impossible to confound the two metals. We shall now proceed to discuss them.

§ 26. The arsenic-mirror, as deposited in the reduction-tube, is highly lustrous, of blackish-brown or brownish-black color, and, when seen against a sheet of white paper, perfectly transparent brown in places where the deposit is not too thick. The antimony-mirror is, next to the heated spot, partly fused to small globules, and there it appears of almost silver-white color; more distant from the flame it is nearly black, and forms, when in very thin layers, not a continuous lustrous brown and transparent coating, but the tube appears, rather, as if dulled by a brownish-black dust.

Antimoneted hydrogen is decomposed at a lower temperature than arseneted hydrogen. Hence it is, that when hydrogen containing some of the former gas passes through the ignited tube, a metallic mirror is deposited before and beyond the heated spot, provided the quantity of the antimoneted hydrogen be not too small. Arseneted hydrogen never produces a mirror before the heated spot.

The arsenic-mirror is easily driven from one place to another, when gently heated in the current of the hydrogen gas. Hereby a considerable quantity of arsenic is carried off with the gas; and, if the latter is allowed to escape unburnt, the characteristic arsenic-odor very distinctly perceived. But if the

gas is kindled, the flame instantly assumes a bluish-white color, and spots are formed on porcelain which is held into the flame.

The antimony-mirror requires for its vaporization a much higher temperature, and, during vaporization, spots on porcelain can only be obtained when the evolution of the gas is very brisk; for in this case alone, the antimony is not completely deposited in the tube. The escaping gas, if not kindled, is perfectly inodorous. Previous to vaporization, the antimony-mirror changes its appearances at the heated spot; it fuses into small lustrous globules, which may, in all cases, be seen with the aid of a lens (Wöhler); arsenic exhibits no sign of fusion.

If the glass-tube containing the arsenic-mirror is cut off and heated in the flame of a spirit-lamp, the characteristic garlic-odor is evolved. The antimony-mirror volatilizes without any odor.

§ 27. The spots which, on incomplete combustion, arseneted hydrogen deposits on porcelain, are blackish-brown and lustrous, and, when in thin layers, translucent, with a brown, or light-brown color. The antimony-spots, if not too thin, are not lustrous, of velvet-black color, and have, usually, a white deposit in the centre; when in very thin layers, they exhibit lustre; but, even then, their color is not brown, but iron-black, or dark graphite-colored, and only at the extreme edges possessed of a brownish-grey tinge.

The arsenic-spots, when moistened with a solution of hypochlorite of soda, are dissolved; the antimony-spots are not affected by the reagent. This is a very excellent distinguishing test, for which we are in-

debted to Mr. Bischoff. The solution of hypochlorite of soda must not contain free chlorine; it is prepared by passing chlorine gas into a solution of carbonate of soda, or by adding a solution of carbonate of soda to strong chlorine-water. A drop of this solution is placed, by means of a glass-rod, near the spot, and then made to flow over it.

If a drop of sulphide of ammonium is placed, by means of a glass-rod, on an arsenic-spot, and gently heated over a spirit-lamp, the spot is completely dissolved. On allowing the liquid to evaporate, which may be accelerated by blowing, a pure yellow residue of sulphide of arsenic remains behind. An antimony-spot, when treated in the same manner, yields an orange-red residue of sulphide of antimony. This is another very characteristic distinguishing test, discovered by H. Rose. If the sulphide of arsenic is moistened with a drop of hydrochloric acid, it remains undissolved, while the sulphide of antimony dissolves very readily; on the other hand, a solution of carbonate of ammonia dissolves the sulphide of arsenic, and acts not on the sulphide of antimony.

Both the spots of arsenic as well as those of antimony disappear when moistened with nitric acid of from 1.26 to 1.3 spec. gr. To the solution thus obtained a solution of nitrate of silver, or of nitrate of silver and ammonia (prepared by adding exactly so much ammonia to a solution of nitrate of silver that the precipitate is re-dissolved), is added, by means of a glass-rod. The liquid is then carefully neutralized with ammonia, which is done by holding a glass-rod, moistened with ammonia, over the spot. If the spot consisted of arsenic, a yellow precipitate of

arsenite of silver will be produced; if it was an antimony-spot, no reaction takes place. Another very important distinguishing test! A drop of strong sulphureted hydrogen water, when added to the solution of an arsenic-spot, produces a lemon-yellow precipitate of sulphide of arsenic; when added to the solution of an antimony-spot, an orange-red precipitate of sulphide of antimony.

The metallic mirror of the reduction-tube shows, of course, the same behavior to reagents as the spots on porcelain.

By these reactions the nature of the arsenic is established beyond any doubt, and all the other tests which have been proposed, and which are much less conclusive, and more exposed to fallacy, are thus made superfluous. For the sake of completeness, however, we will mention some of them.

§ 28. If a piece of phosphorus, moistened with water, is introduced into a porcelain capsule, and the dish containing the spots placed over it, the spots, if consisting of arsenic, disappear very soon; but very slowly, if consisting of antimony.—(*Cottereau.*) This is owing to the formation of ozone, which rapidly oxidizes the arsenic, and affects but slowly the antimony.—(*Schönbein.*) The places from which the arsenic-spots have been removed, powerfully redden a moistened litmus-paper; the places whence the antimony-spots have been removed, have no effect on litmus-paper.—(*Schönbein.*)

If some iodine is introduced into a porcelain capsule, and the dish containing the spots placed over it, the arsenic-spots assume a pale, yellowish-brown color, which changes, on exposure to air, within a few min-

utes, to yellowish-brown. The reaction disappears on continued exposure to air, or on gently heating. Antimony-spots, under the same circumstances, assume a carmelite-brown color, which, on exposure to air, passes into orange, and which is permanent. If the place from which the yellow arsenic-spots have disappeared is moistened with a drop of sulphureted hydrogen water, or if exposed to the influence of sulphureted hydrogen gas, a new yellow spot immediately appears, which is quickly removed on addition of ammonia. The spots of iodide of antimony which, as before mentioned, do not disappear on exposure to air, are converted, by sulphureted hydrogen, into sulphide of antimony, which resists the action of dilute ammonia for a considerable time.—(*Lassaigne.*)

If a drop of bromine is introduced into a porcelain capsule, and the dish, containing the spots, placed over it, the arsenic-spots very soon assume a fine, lemon-yellow color; the antimony spots, within a still shorter period, become orange-red. Both kinds of spots become colorless on exposure to air, and sulphureted hydrogen produces the same reactions as in the preceding case.—(*Slater.*)

A concentrated solution of iodate of potassa imparts to the arsenic-spots a cinnamon color, and soon after dissolves them, while the antimony-spots resist its action for two or three hours. Chlorate of potassa gradually dissolves the spots of arsenic, but not those of antimony. Nitroprussiate of potassa, on the other hand, dissolves the antimony-spots, but not the arsenic-spots.—(*Slater.*)

§ 29. If the tube containing the metallic mirror,

the reduction-tube, is connected with an apparatus which affords dry sulphureted hydrogen gas, the current being so regulated that the quantity of the escaping gas is just sufficient to burn with flame, and heat is applied by means of a common spirit-lamp from without to within, *i. e.*, against the current of the gas, yellow sulphide of arsenic will be formed if the metallic mirror consisted of arsenic, but orange-colored or black sulphide of antimony, if it consisted of antimony.—(*Pettenkofer*, *Fresenius.*)

If, then, the tube is fastened to an apparatus which affords dry hydrochloric acid gas (for which purpose it is only necessary to put some chloride of sodium into a large excess of sulphuric acid, and to apply a gentle heat), and the gas passed through the tube, without heating, the sulphide of antimony entirely disappears; chloride of antimony is formed, which is very volatile in a current of hydrochloric acid gas. If the escaping gas is transmitted through water, the antimony is retained in the latter, and may readily be detected by sulphureted hydrogen and other reagents. Sulphide of arsenic remains under these circumstances perfectly unchanged, not being affected by the gas at common temperature. By sucking a little ammonia into the tube it is again obtained in solution, which may serve for other experiments.—(*Fresenius. Annalen der Chem. und Pharm., vol.* xliii., *p.* 361.)

§ 30. Antimoneted hydrogen causes, like arseneted hydrogen, a dark precipitate in a solution of nitrate of silver. Similar as the action of the silver salt on the two gases may appear at the first glance, a closer examination will show a decided difference. The

oxide of silver oxidizes both the arsenic and the hydrogen of the arseneted hydrogen; metallic silver is, consequently, deposited, and the liquid contains arsenious acid besides the excess of the silver-salt and free nitric acid.* On carefully adding some dilute ammonia to the filtered solution, a yellow precipitate of arsenite of silver will, therefore, be thrown down, either immediately or after addition of some nitrate of silver, in case the latter should be wanting. Of the antimoneted hydrogen only the hydrogen is oxidized by the oxide of silver; the antimony is precipitated with the reduced silver, either alone or in combination with the latter as antimoniet of silver, *the filtered liquid does not contain the slightest trace of antimony*, and ammonia does, of course, not produce any precipitate.

This difference in the behavior of a solution of nitrate of silver to arseneted and antimoneted hydrogen furnishes a very reliable method to distinguish arsenic from antimony; hence, the test with the silver-solution ought never to be neglected. The facility to completely remove the silver from the solution by hydrochloric acid, admits of the application of various other reagents to the liquid even after the characteristic yellow precipitate has been produced. Whether a solution of terchloride of gold possesses any advantages over

[* The mutual decomposition may be thus expressed: in the case of arseneted hydrogen,

$$6\,(AgO\,.\,NO^5) + AsH^3 = 6Ag + AsO^3 + 3HO + 6NO^5;$$

in the case of antimoneted hydrogen,

$$3\,(AgO\,.\,NO^5) + SbH^3 = Ag^3Sb + 3HO + 3NO^5.]$$

the silver-solution, as is asserted by Lassaigne, I have not yet thoroughly examined; but so much I have ascertained, that a gold-solution of acid reaction is not affected by a gas which produced a distinct reaction in a silver solution. It is, probably, necessary that the gold-solution be perfectly neutral.

§ 31. Which and how many of the above-described tests for ascertaining the nature of the reactions afforded by Marsh's process have to be made, entirely depends on the number and character of the reactions produced, whether one or several metallic mirrors have been deposited in the reduction-tube, whether or no spots on porcelain have been obtained at the same time, etc.

If a precipitate was produced in the solution of nitrate of silver, the first operation consists in filtering the liquid and adding to the filtrate, very cautiously, ammonia. The formation of a yellow precipitate proves conclusively the presence of arsenic. The addition of ammonia is best performed in such a manner that only a drop at the time is placed cautiously on the surface of the liquid, when two strata of different densities are formed, the upper of an alkaline, and the lower one of an acid reaction. The formation of the precipitate takes place at the plane of contact of the two strata, and by very gradually and carefully mixing the two strata it is not difficult to add just sufficient ammonia to make the precipitate permanent. The precipitate of arsenite of silver thus obtained may be treated with hydrochloric acid; the latter removes the silver, and from the solution the arsenic may be precipitated by sulphureted hydrogen; the sulphide

of arsenic may be collected on a filter, dissolved in ammonia, the solution evaporated, and the residue treated with carbonate of soda and cyanide of potassium after the method of Fresenius (v. § 35).

If, besides the metallic mirror, spots on porcelain have been obtained, these must now be made the object of further experiments. A drop of nitric acid of from 1.26 to 1.3 spec. gravity is placed, by means of thin glass-rod, on one of the thickest spots. If, after a few minutes' action, complete solution should not have been effected, a little more acid is added. Application of heat is only required when a weaker acid has been used. In a similar manner a drop of nitrate of silver and ammonia is then added, when the characteristic yellow precipitate is produced, either immediately or after addition of a trace of ammonia, if the spot consisted of arsenic (v. § 27). This decisive experiment must be executed with the greatest care, and requires considerable skill in chemical manipulations. Instead of a solution of nitrate of silver and ammonia, which must be free from an excess of ammonia, a solution of nitrate of silver may be employed, and afterwards ammonia be added, or a glass-rod, moistened with ammonia, be held over the liquid.

If there is reason to apprehend that too much nitric acid was used to effect the solution of the spot, the porcelain may be very gently heated, and the excess of acid be removed by carefully blowing on the drop. In this case, *i. e.*, in the case of an excess of nitric acid, some arsenic acid may have been formed, and on addition of nitrate of silver, a reddish or brownish precipitate may appear; it consists of a

mixture of arsenite and arsenate of silver. To prevent the adhesion of too large a portion of the liquids to the glass-rods, these should be chosen very thin, or better still, be substituted by glass-tubes, very narrowly drawn out at one end; from these the solutions can be made to flow out in very small drops.

The second experiment consists in moistening another spot with a solution of hypochlorite of soda; if it is dissolved, it is an arsenic spot; if not, an antimony spot (v. § 27). If both metals should happen to be present, the arsenic, being the more volatile metal, occupies the outer edge of the spot; and, on adding the reagent, the outer brownish-black part only disappears. If only a small quantity of antimony occurs with the arsenic, the whole of the spot is dissolved (*Wackenroder*). It is an important feature of this test, that it can be practised on the very thinnest spots, while the silver reaction requires much thicker spots to become apparent.

Another spot, which must not be too thin, may be dissolved in nitric acid, in the manner above described, and the solution mixed with a drop of freshly prepared and very concentrated suphureted hydrogen water. If the spot consisted of arsenic, a pure yellow precipitate of sulphide of arsenic is thrown down, while the precipitate is of an orange color if it consisted of antimony. This experiment may be followed by the important test with sulphide of ammonium (v. § 27).

The examination of the spots, after the methods of Cottereau, Lassaigne, and Slater, should only be performed if there is a sufficient number of them.

§ 32. Considerable importance is attached to the chemist's placing an arsenic mirror, as a *corpus delicti*, in the hands of the authorities. For this reason, the analyst should always endeavor to obtain two mirrors, the one to be disposed of as mentioned, and the other to serve for further experiments. If only one mirror could be procured, there remains nothing but to divide it. The glass tube is divided by the cut of a sharp file at the middle of the mirror, and broken. For this division, the drawing out of the tube, as described in § 12, offers great conveniences, because, in this arrangement, the mirror is distributed over a larger surface. In using these tubes, it is not even necessary to prepare two mirrors, because the division, if made at the middle of the narrow part, furnishes two very fine mirrors, each of which is usually much more distinct than any one deposited in a common wide tube.

The first experiment to be made with the mirror, consists in holding that end of the tube where the metal is deposited, into a very small flame of a common spirit lamp (v. § 4). If the mirror consists of arsenic, the flame assumes a bluish-white color, and the alliaceous arsenic odor is evolved; the odor is very distinctly perceived when the heated tube is quickly held under the nose. This peculiar smell is alone sufficient to prove undoubtedly the presence of arsenic. This experiment, also, is best performed with a tube that has been drawn out, and afterwards been cut at the narrow part, because the thin tube becomes sufficiently heated by the very smallest flame, and but a small portion of its contents is lost.

The mirror is now dissolved in nitric acid for further examination, and the solution tested with nitrate of silver. To effect solution, a drop of nitric acid is placed into a small porcelain dish, and cautiously sucked up into the tube containing the mirror. The metal dissolves readily if the acid is of the proper concentration; by blowing into the tube, the drop is brought back into the dish. The tube may be washed out with a drop of water, by proceeding in the same manner. The examination with nitrate of silver is executed in exactly the same way as prescribed for the examination of spots in § 27. If there is a sufficient quantity of the solution, a portion is tested with sulphureted hydrogen water; and, if there is no lack of material, the behavior of the mirror to hypochlorite of soda may be ascertained (v. § 27).

If the experiments are strictly executed after the manner described, there can no longer remain any doubt as to whether the reactions obtained by the process of Marsh were produced by arsenic, or antimony, or by a mixture of both metals. In the last, and more complicated case, it is very desirable to apply, if possible, the test proposed by Fresenius, as above (§ 29), described; viz.: to treat the metallic mirror in a current of sulphureted hydrogen, and to treat the sulphide thus formed with gaseous hydrochloric acid. If antimony has been found, inquiries should be instituted as to whether antimonials have been administered as a medicine, and, if both antimony and arsenic have been detected, it will be necessary to test the antimonial for an admixture of arsenic.

§ 33. We will now consider the method of reduction of Fresenius and Babo. It is based on the observation, that the sulphides of arsenic, the arsenites and arsenates, when fused with a mixture of cyanide of potassium and carbonate of soda, yield metallic arsenic; and that this metal is obtained in the shape of a lustrous mirror in all cases where the base of the salt is not at the same time reduced, or, if it suffer reduction, where an arseniuret is formed, which, on application of heat, parts with all or part of its arsenic. In reducing a sulphide of arsenic in this manner sulphocyanide of potassium is formed, and in reducing an arsenite or arsenate the cyanide of potassium is changed to cyanate of potassa.

Fresenius recommends the use of the sulphide of arsenic as obtained by the treatment of the crude sulphide with nitric and sulphuric acid, extraction of the mass with water, and precipitation of the solution with sulphureted hydrogen (§ 14). The precipitate is collected on a filter, washed, dissolved in ammonia, and the solution evaporated in a porcelain dish. The dish with the sulphide of arsenic may be dried, over a water-bath at 40°C, and the weight of the sulphide before reduction be ascertained, whence the weight of the arsenic or arsenious acid may be deduced.

It has already been mentioned (§ 14), that by proceeding in this manner the sulphide of arsenic is not always with certainty obtained perfectly free from organic matter, even by a skillful operator. For this reason I consider it much more appropriate to employ the pure sulphide of arsenic as resulting from the treatment of the crude sulphide with nitric acid,

subsequent fusion of the residue with nitrate and carbonate of soda, etc. (§ 12), and which is perfectly free from organic substances. The sulphide of arsenic obtained after this method is collected on a filter, washed, dissolved on the filter in ammonia, and the solution evaporated in a porcelain dish. Its weight may then, if necessary, be determined; it is sure to be the tersulphide AsS^3; 100 parts correspond to 80.4 of arsenious acid, and to 60.9 of metallic arsenic.

H. Rose has observed, that in fusing sulphide of arsenic with cyanide of potassium, not the whole of the arsenic becomes reduced, but that part of it forms a sulpho-salt, which is not acted upon by cyanide of potassium. If the sulphide of arsenic contains a certain amount of sulphur, no reduction whatever is effected; hence the tersulphide affords a greater quantity of reduced arsenic than the pentasulphide. The reduction of the arsenic acid to arsenious acid by means of sulphurous acid (§ 13), ought, therefore, not to be neglected.

It has been stated before, that cyanide of potassium reduces the whole of the arsenic from arsenic and arsenious acids; hence, the most rational way of procedure appears to be the conversion of the pure sulphide of arsenic, obtained in the manner just described, into arsenic acid, and the application of this compound for the process of reduction. Concentrated nitric acid is added to the sulphide of arsenic, contained in the porcelain dish, and the acid evaporated by heat; this is repeated several times, if necessary; to remove the last traces of nitric acid, the mass is repeatedly moistened with water, and

evaporated to dryness; the final residue is again softened with water, some dry carbonate of soda added, so that an alkaline mass is formed, and the whole again evaporated to a perfectly dry mass, which now is eminently adapted for the process of reduction.

§ 34. The apparatus of reduction, as constructed by Fresenius and Babo, is represented in Fig. 6. (A)

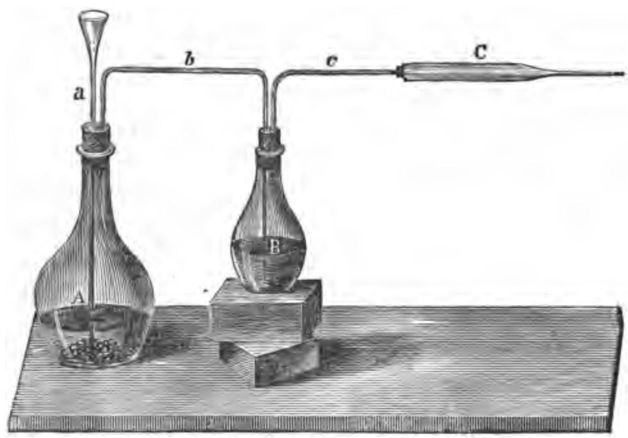


Fig. 6.

is a large gas-bottle, for the preparation of carbonic acid. It is filled to about one-half with water and large pieces of marble or compact limestone; chalk should not be taken, since it does not afford a constant current. A funnel tube (a) passes through one of the apertures of the doubly perforated cork to near the bottom of the flask. Into the other aperture, a tube (b) is inserted, which conducts the gas into the small bottle (B), partially filled with concentrated sulphuric acid, by which the gas is at once

washed and dried. Through the tube (c), the carbonic acid passes into the reduction-tube (C), represented in Fig. 7.

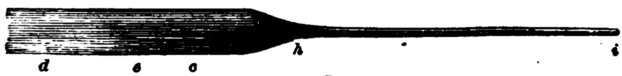


Fig. 7.

The apparatus having been arranged, the sulphide of arsenic (or, better still, the mass obtained by neutralization with carbonate of soda, and in which the arsenic is in the shape of an arsenite or arsenate), is mixed in a heated mortar—a mortar of agate is preferable to any other kind—with about ten parts of a pulverized and well-dried mixture of three parts of anhydrous carbonate of soda, and one part of cyanide of potassium; the powder is placed on a narrow strip of smooth paste-board, which is bent up at the sides, and pushed into the reduction-tube down to (e). By turning the tube, the mixture is placed at (d e), without soiling any other portion of the tube. The pasteboard is then carefully removed.

The tube, when filled in this manner, is fitted over the cork of the tube (c) of the apparatus.

Hydrochloric acid is now poured through the funnel-tube to produce a moderate current of carbonic acid gas, and *the mixture carefully dried*, which is done by very gently heating the tube throughout its whole length by the flame of a spirit-lamp. When every deposition of water has disappeared, and the current of gas become so slow that only one gas-bubble passes through the sulphuric acid every second, the reduction-tube is heated to ignition at the place (c). When this point is reached, heat is

also applied to the mixture, beginning at (d), and slowly progressing towards (e) until the whole of the arsenic is driven off.

The reduced arsenic is deposited at (h), while a very small portion makes its escape at (i), and imparts to the air its peculiar alliaceous odor. Towards the end of the operation the second lamp is gradually advanced to (c), and thus the arsenic, which is deposited in the wider part of the tube, driven to (h). This done, the tube is closed at the narrow end, and the mirror driven by heat from (i) to (h), when it presents a very fine and purely metallic appearance. The tube is then cut off at (e), the open end closed with a cork, and deposited *ad acta.*

In driving the arsenic from one place to another, the greatest circumspection must be observed, since a loss of arsenic is almost invariably experienced, even if the current of the gas is very feeble. It would appear that the gaseous arsenic is much less easily deposited from the heavy carbonic acid gas than from the light hydrogen gas. I have already (§ 16,) had occasion to observe that, in my opinion, the presence of a very small quantity of arsenic cannot so conclusively be demonstrated by this process as by the process of Marsh.

The presence of the compounds of antimony in the mass subjected to reduction, does, in the process of Fresenius and Babo, not influence the result, because not a trace of the reduced antimony is volatilized, and because the reduced antimony does not retain the arsenic. This is a great advantage of the process in question; it excludes the possibility of mistaking antimony for arsenic. The presence of tin also does

not interfere with the result, and other metals, besides antimony and tin, cannot very well occur.—(Compare *H. Rose*, Pharm. Centralblatt, 1853, p. 593, and Handbuch der analytischen Chemie).

§ 35. The reduction of sulphide of arsenic and arsenates, by means of cyanide of potassium, may very conveniently, and in a very simple manner, be executed in a glass-tube, as represented in Fig. 8.

Fig. 8.

The arsenical mass, after having been perfectly dried, is placed in the bulb, and the pulverized and dessicated mixture of cyanide of potassium and carbonate of soda added. The bulb must not be more than about half full. The narrow part of the tube is then carefully cleaned by means of some blotting-paper, wrapped round a knitting-needle. Heat is next applied to the bulb, just sufficient to drive out the last trace of water, which escapes and is removed with blotting-paper. When the narrow portion of the tube appears perfectly dry and clean, and has become sufficiently cool, the temperature of the bulb is raised to cause fusion of its contents; this temperature is kept up for some time. The reduced arsenic sublimes, and forms in the narrow part of the tube a mirror of great purity, provided the tube was carefully cleaned and dried. (Fig. 9).

Fig. 9.

I recommend to increase the heat, towards the end

of the operation, by means of the blow-pipe, when a very excellent arsenic-mirror will be obtained. In case one should be disinclined to use sulphide of arsenic for this reduction, the residue contained in the porcelain dish (§ 33), and which is free from nitric acid, may be saturated with lime-water, instead of carbonate of soda, when, on evaporation, a pulverulent lime-salt is obtained, which mixes very easily with cyanide of potassium and carbonate of soda.

The reason why Fresenius and Babo did not recommend this simple method of reduction is very apparent. The volatilization of the arsenic takes place, in this case, in atmospheric air, and traces of the metal may, therefore, escape detection, in consequence of oxidation. Hence, the use of the above described apparatus, where the volatilization of the arsenic is effected in a current of carbonic acid gas. A better success might, perhaps, be secured by adding a small quantity of a body which affords carbonic acid, ex. gr. carbonate of lime.

§ 36. We now come to the third of the cases enumerated in § 3.

Experiments, conducted by Orfila, Meurer, and other chemists, have shown that arsenic, when introduced into the stomach, is absorbed and carried by the blood into most other parts of the body, where its presence may be detected even if it can no longer be found in the stomach and the intestines. Meurer and Prinz gave to a horse half a drachm of white arsenic daily, in the shape of a bolus; four such doses were given, and thirty hours after the application of the last dose, the horse was killed.

No symptoms of poisoning had shown themselves,

and not a trace of arsenic was found in the stomach; but the poison was detected in the blood, in the urine, and in the liver of the animal.

It is, therefore, required, in cases of suspected poisoning, to analyze, if necessary, the urine, the blood, the liver, the bile, and other liquid and solid portions of the body, since it is quite possible that, after removal of the greater part of the poison by vomiting and purging, the rest may have passed from the *primæ viæ* by absorption into the liquid and solid portions of the body.

The urine may be acidulated with hydrochloric acid, either without further preparation, or after having been concentrated by evaporation, and then treated with sulphureted hydrogen, as described § 10. Or it may be evaporated to dryness, and the residue be treated with hydrochloric acid and chlorate of potassa, as described § 9.

The blood and the organs, as liver, kidneys, etc., (the latter after having been cut into small pieces), are also treated with hydrochloric acid and chlorate of potassa, to effect as complete as possible a destruction of the organic matters, and the resulting liquid is subjected to the same processes as those given for the examination of the contents, food, etc., in the second case.

§ 37. The chemico-legal examination is, in the highest degree, laborious and disgusting, when the body to be examined has been interred for months or years, and has passed into a state of putrefaction. In such a case, it is frequently no longer possible to distinguish or separate individual organs, and the analyst is then necessitated to examine the whole

mass of putrefied organs, or the whole of the soft parts which dry up under some particular local circumstances, and even the bones. When this is the case, the body should not be laid in a bath of chlorine-water, or solution of chloride of lime, in order to destroy the offensive odor, since arsenic may thereby be extracted and lost. If chlorine-gas is employed to disinfect the body, it must be evolved by means of distilled sulphuric acid, free from arsenic. All soft parts, especially those which may have formed parts of the abdominal viscera, are carefully separated from the bones, and treated with hydrochloric acid and chlorate of potassa, as in the second case.—(*Wöhler* and *Von Siebold*).

§ 38. The following is another convenient process, given by Wöhler and Von Siebold, much to be prepreferred for the treatment of bodies which have been exhumed entire after some month's interment.

The entire soft parts are treated, in a large dish of genuine porcelain, with moderately strong nitric acid, which has been previously tested for arsenic; the dish is then heated upon a sand-bath, and its contents well-stirred, until the organic matters are so far destroyed and dissolved as to form a homogeneous pasty mixture. This is now neutralized with a solution of pure hydrate or carbonate of potassa, and about as much finely-powdered nitre (previously tested) added, as is equal in weight to the soft parts. The whole is now evaporated to dryness, with constant stirring, and the dry mass introduced by degrees, in small portions, into a new clean Hessian crucible, heated to dull redness. In this manner, the whole of the organic matter is burnt, and the

arsenic, if present, converted into arsenate of potassa. In this process, it is important, and not very easy, to add the proper quantity of nitre. If too little nitre is employed, part of the organic matter may remain unburnt, and arsenic may be volatilized from the carbonaceous mass; on the other hand, too much nitre would interfere with the subsequent treatment of the mass. It is better to make a preliminary test with a small portion of the mixture, by introducing it into a small red-hot crucible, and observing whether the mass is perfectly white after deflagration. If it is black and carbonaceous, more nitre must be added.

The mass, which now consists essentially of carbonate, nitrate, and nitrite of potassa, and may, also, contain arsenate of potassa, is dissolved in the smallest possible quantity of boiling water, and the solution, without filtering off from the suspended phosphate of lime and silica, gradually mixed, in a porcelain dish, with a slight excess of sulphuric acid. The pasty saline mass, thus produced, is carefully heated till all the nitric and nitrous acid is expelled, a point to which great attention must be paid. On cooling, the mass is stirred up with a little cold water, and the solution poured off from the large deposit of sulphate of potassa. The latter is washed several times with cold water, the washings mixed with the first solution, the liquid boiled with sulphurous acid, and sulphureted hydrogen gas passed through it for several days, while, from time to time, a gentle heat is applied. The subsequent operations are the same as in the second case.

§ 39. For the sake of completeness, the following

remarks on some other methods of detecting arsenic in medico-legal cases, including some of the older processes, mày here find their place.

Instead of treating, as in the second case, and as described § 9, the food, the contents, etc., with hydrochloric acid and chlorate of potassa, I have formerly recommended to digest the substances in a porcelain dish with water, strongly acidulated with hydrochloric acid; the temperature, which, at first, must be very gentle, is gradually increased till near the boiling point, and even raised to boiling if the liquid should not have become sufficiently clear and limpid to admit of a rapid filtration. Arsenious acid, if present, dissolves readily in the acidulated water; starch, if present, is converted into dextrine and sugar; albumen and albuminous substances are coagulated or dissolved; in short, the whole is liquefied. The residue, after having been separated from the liquid by filtration, is treated in the same manner with acidulated water; the liquid portion is again filtered off, and both filtrates are mixed together. Through this solution a current of sulphureted hydrogen is passed (§ 10), and the arsenic, if present, precipitated as sulphide. If, from the liquid, thus treated, no precipitate is deposited, even after twenty-four hours' resting, it is sure to form on evaporation; evaporation, therefore, ought never to be omitted. The liquid, having arrived at that point where the precipitate begins to appear, is again treated, after cooling, with sulphureted hydrogen, to effect a complete separation of the arsenic. The precipitate is collected on a small filter, dissolved in ammonia, and subjected to the treatment described § 11.

If the treatment with hydrochloric acid should not happen to afford a liquid fit for filtration, I recommend to strain the liquid through cloth, and to pass through the filtrate a continued current of washed chlorine-gas, until it has become clear, and of wine-yellow color. The chlorine is then expelled by heat, and the liquid treated, after cooling, with sulphureted hydrogen.

Fresenius and Babo have raised against this method (the treatment with hydrochloric acid), the well-founded objection, that a perceptible quantity of terchloride of arsenic is volatilized on boiling a solution of arsenious acid in water, containing hydrochloric acid, and that, if the arsenic is present as sulphide, it does not enter, or only partially enters, into solution.

§ 40. Drunty proposed to remove the organic matter from the extract, óbtained by treating the substances under examination with acidulated water, by means of alcohol, and Brandes corroborated its usefulness for this purpose. On this, Duflos and Hirsch founded their method, described in the above cited work (§ 3, note), which consists in introducing the organic substances, previously cut into shreds, into a tubulated retort, and adding pure hydrochloric acid of 1.08 spec. gr., about equal in weight to the solid portion of the masses. A receiver, containing about an ounce of water, is attached to the retort, and the latter heated in a chloride of calcium bath. Ebullition is kept up until the greater portion of the liquid part of the contents of the retort have passed over; in other words, until the residue becomes thick and pasty. The retort is allowed to cool, the receiver

removed, and the residue mixed with twice its own weight of alcohol. After a while, the mass is thrown on a cloth, and the residue repeatedly washed with alcohol; the liquid is then filtered, the filtrate introduced into a retort, and the alcohol distilled off. What now remains in the retort is mixed with the first acid distillate, which may contain traces of chloride of arsenic, and the whole, after cooling, treated with sulphureted hydrogen. The objections to this method are, that it does not effect solution of the sulphide of arsenic, and that it does not possess any particular advantage.

§ 41. Graham effects the removal of the organic substances, held in solution, by means of nitrate of silver. The masses under examination are boiled with water, acidulated with a few drops of nitric acid, then strained through a cotton or woollen cloth, and the filtrate mixed with nitrate of silver, until all organic matters are precipitated. The excess of the silver is removed by chloride of sodium, and the filtrate treated with sulphureted hydrogen. This process has the same disadvantage as the preceding; besides, to effect the separation of a liquid containing chloride of sodium from chloride of silver by filtration, is rather precarious.

§ 42. Danger and Flandin destroy the organic matter by concentrated sulphuric acid. The substances are mixed in a porcelain dish with from one-sixth to one-fourth of their own weight of concentrated sulphuric acid, and heat applied. The action of the acid on the organic substances consists in converting them into a black, pasty mass, which, with continued heating, assumes the appearance of a dry

charcoal. On reaching this point, the dish is allowed to cool; to the cold mass a little concentrated nitric acid, or aqua regia, is added, and the whole again evaporated to dryness. The residue, on being treated with boiling water, affords a limpid liquid, in which the arsenic, if present in the original substances, occurs as arsenic acid; the liquid may be poured into Marsh's apparatus, or may be treated with sulphureted hydrogen, in order to obtain sulphide of arsenic. The sulphuric acid ought to be pure, and, if the liquid is to be tested in Marsh's apparatus, particular care ought to be taken to completely remove the nitric acid by evaporation.

The method of Danger and Flandin has more especially been recommended for the examination of the solid organs, as the liver, kidneys, etc., but can, of course, also be employed for the analysis of the contents, food, etc., and blood, bile, etc., after previous evaporation. Owing to the treatment of the dry mass with nitric acid, the arsenic, in this process, is carried into solution, even if it was present as sulphide; but experiments have shown, what might have been *à priori* expected, that, under the treatment with sulphuric acid, a loss of arsenic, in the shape of terchloride, is experienced, if chloride of sodium, or other chlorides, are present; and the perfect absence of these is perhaps never to be expected. Orfila and Jacquelin obtained, for this reason, always less arsenic in operating after this method, than after effecting the destruction of the organic matters by means of chlorine gas. The process, it is true, is very simple and very convenient. I have obtained myself, in following it, very pure solutions from

organs, food, etc., but the defect above stated, makes it much inferior to the process recommended by us.

§ 43. Founded on the observation that arsenic is volatilized as terchloride, when substances containing arsenious acid are heated with hydrochloric acid, or, what amounts to the same, with chloride of sodium and sulphuric acid, a new method for the detection and separation of arsenic, in chemico-legal cases, has been proposed. The substances under examination (food, contents, vomited matters) are placed in a tubulated retort, and a large quantity of chloride of sodium and sulphuric acid added, of the latter not quite sufficient to effect complete decomposition of the salt; the receiver must be well cooled. The distillate contains terchloride of arsenic, if arsenious acid was present. It is essential that the distillation should be carried on for a considerable time, because the greater portion of the chloride of arsenic passes over towards the end of the operation, when the temperature is higher than at the beginning, owing to the more concentrated state of the liquid. An excess of sulphuric acid has to be avoided, because it gives rise to the formation of sulphurous acid, which makes the distillate impure, and unfit to be tested after Marsh's method. Schneider recommends the use of pieces of fused chloride of sodium, or rock-salt, and a gradual addition of the sulphuric acid during the process of distillation, to be poured through a tube with an ∞ shaped bend in the middle. This arrangement permits a concentration of the contents of the retort by distillation, previous to the addition of the acid, if too much water should happen to be present.—(*Schneider*, Lie-

big's Jahresbericht, 1851, p. 620; *Fyfe*, Journal für pract. Chemie. Bd. 55, p. 103.)

Different ways have been proposed for the further treatment of the distillate thus obtained. It is either to be introduced, without further preparation, into Marsh's apparatus, or to be treated with sulphureted hydrogen, or to be tested with nitrate of silver. Being strenuously opposed to introducing liquids containing hydrochloric acid into the apparatus of Marsh, I cannot recommend the first of these methods. The large quantity of hydrochloric acid which is present in the distillate requires, at all events, a very gradual addition. Volatile organic bodies, formed by the action of the hydrochloric acid on the organic matters, and which always occur in the distillate, contribute, besides, to influence the accuracy of the result. Nor is the proposal of Fyfe, to test the distillate with nitrate of silver, a very recommendable one, considering the large amount of nitrate of silver which has to be added to remove the chlorine, the consequent accumulation of nitric acid in the liquid, and the formation of a considerable quantity of nitrate of ammonia on neutralizing the free acid with ammonia. The precipitation of the arsenic by means of sulphureted hydrogen, appears to be, after all, the best way. But this is, according to my experience at least, not very easily accomplished, on account of the presence of the organic matters; the liquid assumes a dark yellow color, and, if only a minute quantity of arsenic is present, the sulphide is but very slowly deposited. This process, finally, possesses, in common with many other methods, the disadvantage of leading exclu-

sively to the detection of arsenic, and not, at the same time, to the detection of other poisonous metals; it is only antimony and, perhaps, tin, that may also distill over, as chlorides, into the receiver.

§ 44. At an earlier period, it was recommended to treat the organic substances with caustic potassa, in order to extract the arsenic. The food, contents, etc., were boiled with a solution of caustic potassa, and the liquid afterwards acidulated with hydrochloric acid; the albuminous bodies are thereby precipitated in a finely divided state. After this method, an acid liquid is obtained, which is always very rich in organic matter, and in which sulphureted hydrogen produces a copious precipitate, even if not a trace of arsenic is present. It should also be borne in mind that, on boiling albuminous substances with caustic potassa, sulphide of potassium is formed, which, on being decomposed with hydrochloric acid, gives rise to the formation of sulphureted hydrogen; this acts on the arsenious acid which has entered into solution and precipitates sulphide of arsenic. In an experiment, conducted after this method, I failed to detect the arsenic. In the opinion of Pettenkofer, the sulphide of potassium becomes readily oxidized on exposure to air; still, he recommends, as the safer method, to treat the alkaline solution with some carbonate of lead, which removes the sulphur.

§ 45. Another method prescribed to boil the organic substances with a solution of caustic potassa until as complete as possible a solution was obtained, to acidulate the liquid with hydrochloric acid, and to pass chlorine-gas through it until the whole of the organic matters were destroyed; that is, until the

liquid, after twenty-four hours resting in a covered vessel, smells of free chlorine. The excess of chlorine, and the hydrochloric acid formed during the process, should then be driven off by heat, and the liquid be treated with sulphureted hydrogen. To this method it must be objected that the treatment with chlorine-gas is an exceedingly laborious operation, which is very conveniently substituted by the treatment with chlorate of potassa, as given § 9, and that some arsenic may be lost in the evaporation of the acid liquid.

§ 46. Since sulphureted hydrogen precipitates the arsenic completely from its solution, even in presence of ammoniacal salts and organic substances, there is no longer any doubt entertained that sulphureted hydrogen gas is the best precipitant for arsenic from a solution, prepared after any of the previously mentioned methods. What speaks, moreover, in favor of the reagent is the circumstance that it throws down, at the same time, other poisonous metals which may be present, and which might have caused the death of the individual. The method of Valentin Rose, which I shall now notice, and in which lime-water is used for the precipitation of the arsenic, has, therefore, only a historical interest. The substances under examination are boiled with a very dilute solution of caustic potassa (one part of caustic potassa to forty-eight of water), the liquid is filtered through cloth, the filtrate heated to ebullition, and, while in this state, mixed with nitric acid, in small portions, until a fresh addition causes no longer a separation of solid matter, and until the liquid shows a strong acid reaction, and has become limpid and of a pale yellow color. When cold, the

liquid is filtered through paper, the filtrate mixed with carbonate of potassa, almost to the point of neutralization, and boiled to remove the carbonic acid. To the limpid liquid of feebly acid reaction, lime-water is added in excess, and the whole heated to ebullition, to facilitate the deposition of the precipitate, which consists of arsenite and phosphate of lime, together with some organic matter. But the presence of organic matter, and of salts, especially sal ammonia, prevents the complete precipitation of the arsenite of lime, and hence it is that small quantities of arsenious acid cannot be detected by this method.

§ 47. Arsenate and arsenite of lime are very good materials for the production of arsenic-mirrors, but the precipitate obtained in the manner prescribed by Valentin Rose, is not fitted for this experiment, on account of the organic matter which it contains. The lime-salt must be precipitated from solutions which are free from such substances.

A liquid, well adapted for this purpose, may be obtained by repeatedly treating the crude sulphide of arsenic with nitric acid; or, better still, by carefully digesting the crude sulphide with hydrochloric acid, with occasional additions of chlorate of potassa. The resulting liquid is mixed with a solution of caustic potassa until it shows a weak alkaline reaction, and then precipitated with freshly prepared lime-water; the whole is heated to ebullition, when the arsenate of lime becomes granular, and settles easily to the bottom.

If there is a sufficient quantity of the precipitate, it may be collected on a filter and washed; but, if

the amount is very small, it must be washed by decantation. In this case, the hot liquid with the precipitate is poured into a conical-shaped glass, and the precipitate allowed to settle; the clear liquid is then drawn off by means of a pipette, hot water, to which some lime-water has been added, poured on the sediment, and, after a while, drawn off again. If necessary, the process is once more repeated. The portion of the liquid which remains in the glass after the last decantation, and which contains the precipitate in suspension, is transferred into a porcelain dish, or a watch-crystal, and evaporated to dryness.

The reduction is effected in the following manner: the residue, or the precipitate from the filter, is mixed with some freshly ignited charcoal-powder, and the mass placed in the bulb of the reduction-tube (Fig. 9, p. 59); the tube is cleaned in the manner described § 35, the mixture carefully dried, and then the bulb heated to redness, by means of the flame of a spirit-lamp and the blow-pipe.

If the mixture was properly dried, and the tube clean, a very excellent mirror is produced. The compounds of antimony afford, under the circumstances, no mirror; the appearance of the mirror is, therefore, a conclusive proof for the presence of arsenic. The mirror, after having been cut off, may serve for other experiments. A mixture of cyanide of potassium and carbonate of soda answers still better than charcoal; the reduction is then executed as taught § 35.

§ 48. Instead of precipitating arsenic acid with lime-water, it is much to be preferred to effect the precipitation of the acid by means of a soluble salt

of magnesia, and ammonia. The liquid is mixed with ammonia in excess, then chloride of ammonium and, subsequently, sulphate of magnesia added. A crystalline precipitate of arsenate of magnesia-ammonia is thrown down, which is washed on a filter or in a glass, with ammoniacal water. It is dried and used for reduction. This precipitate, as well as the arsenate of lime, may, also, very advantageously, be used for Marsh's test; it is, for this purpose, dissolved in dilute sulphuric acid.

§ 49. The use of arsenate of lime for the preparation of an arsenic mirror, has also been recommended by Berzelius. This chemist prepared the solution, requisite for the precipitation, in the following manner: the purified sulphide of arsenic, as resulting from the evaporation of the ammoniacal solution (v. § 11), is removed from the small porcelain dish, or watch-crystal, by mixing and rubbing it with a little pulverized nitre. Another portion of nitre is then fused in a porcelain crucible, or in a glass-tube, and the mixture of sulphide of arsenic and nitre added in small portions to the fused mass; the oxidation is thus rapidly effected. The fused mass which contains arsenate, carbonate, sulphate, nitrate, and nitrite of potassa, is dissolved in a small quantity of hot water, and the solution mixed with an excess of freshly prepared lime-water; the mixture is heated to ebullition, and then treated as above described. It is this method, as will be seen on comparison, which Meyer employed to effect the destruction of the organic matters in the crude sulphide of arsenic, substituting only nitrate of soda for common nitre, and adding carbonate of soda to remove any anti-

mony which might be present. The fused mass, thus obtained, contains a considerable quantity of alkaline carbonate; it is dissolved in water, the solution acidulated with nitric acid (not sulphuric acid, to prevent the formation of sulphate of lime), heated to ebullition (to drive out the carbonic acid), and precipitated with lime-water. If it is intended to precipitate the arsenic acid with a salt of magnesia, sulphuric acid may be taken instead of nitric. I must again repeat that there is no better method for the destruction of the organic matters.

§ 50. At a later period, Berzelius proposed the use of the sulphide of arsenic for the production of arsenic-mirrors. The method of reduction which he recommended, gave results, surpassing in delicacy and accuracy, all others hitherto known for the detection of arsenic in legal investigations. The sulphide of arsenic resulting from the evaporation of the ammoniacal solution (v. § 11), is mixed, while still moist, with dry carbonate of soda, and the mixture formed into the shape of a small cylinder, a little water being added, if necessary. The cylinder is dried at a very gentle heat, and placed, by means of a glass-rod, at the point (d) of the reduction-tube (c) of the apparatus. (Fig. 10.)

The apparatus consists of a gas-bottle, for the evolution of hydrogen gas from zinc and dilute sulphuric acid, a tube (a) filled with loose cotton, and a chloride of calcium tube (b). The reduction-tube, made of glass of tolerable thickness, is connected with the latter by means of a cork, as shown in the figure. The different parts of the apparatus having been joined together, some moderately diluted sul-

phuric acid is poured through the funnel-tube on the zinc and water, previously introduced into the bottle, and thus a current of hydrogen gas of moderate velocity produced. As soon as the air is completely driven out, the reduction-tube is very gently heated at (d) and before this point, by means of a common spirit-lamp, and thus the complete dessication of the mass very readily effected. The moisture collects beyond the point (d), and is easily removed from the tube by application of the flame.

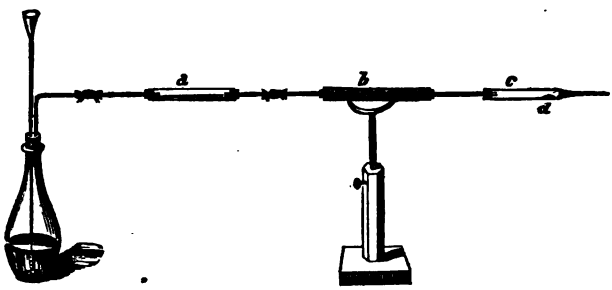


Fig. 10.

When the mass has become perfectly dry, and the reduction-tube, beyond the point (d), sufficiently cool, the place (d) is heated with a powerful flame, when a beautiful mirror of metallic arsenic will be deposited beyond this spot, as illustrated by Fig. 7, (p. 57).

H. Rose, in his investigations on the action of alkaline carbonates on sulphide of arsenic, gives the following explanation of the formation of the metallic mirror. The humid mixture of tersulphide of arsenic and carbonate of soda contains arsenite of soda and sulpharsenite of soda, resulting from the

mutual decomposition of soda and sulphide of arsenic to sulphide of sodium and arsenious acid ($3\ NaO + AsS^3 = 3\ NaS + AsO^3$), the former entering into combination with the sulphide of arsenic, the latter with the soda. On applying heat, both compounds give off arsenic, the arsenite being thereby converted into arsenate, and the sulpharsenite into sulpharsenate ($5\ AsS^3 = 3\ AsS^5 + As^2$).

Besides, the arsenic acid of the arsenate becomes reduced by the hydrogen, and thus increases the amount of free arsenic. It was formerly supposed, and I shared this opinion, that the sulphosalt was also decomposed by the hydrogen, that a sulphohydrate was formed, and arsenic liberated. But this is, according to H. Rose, not the case; the sulphosalt remains unchanged, and hence only part of the arsenic is obtained.—(Pogg. Annalen. Bd. 90, p. 565; Pharm. Centralblatt. 1854. p. 46.*)

However this may be, there is this objection to be raised against the method of Berzelius, that the reduced and vaporized arsenic is never completely deposited in the tube, but that a portion of it is always carried off with the current of the gas. This becomes very evident if the gas is kindled before the process of reduction has commenced; the flame is the ordinary hydrogen-flame; but, as soon as re-

* If a mixture of dry tersulphide of arsenic with carbonate of soda is heated, arsenate and sulpharsenate of soda are formed, and arsenic set free ($5\ AsS^3 = 3\ AsS^5 + As^2$); but, if the pentasulphide is heated with carbonate of soda, the arsenate and sulpharsenate are formed without liberation of arsenic. If the operation is performed in a current of hydrogen gas, the last-named mixture also affords an arsenic-mirror, owing to the reduction of the arsenic acid.—(*H. Rose.*)

duction takes place, the characteristic white coloration of the flame becomes apparent, and, if a porcelain dish is held into it, very beautiful spots are deposited. This circumstance is by some considered as an advantage of the method, since it affords, like the method of Marsh, not only a metallic mirror, but at the same time the characteristic spots. As early as 1830, the white color of the flame in this process was noticed by Wackenroder, and considered very characteristic; he collected the arsenious acid in a closed glass-tube, held over the flame, to be subsequently tested with sulphureted hydrogen.

Since the amount of escaping arsenic increases with the velocity of the current, the evolution of gas should be very moderate. I was formerly of opinion that the arsenic passed off as arseneted hydrogen, but this Fresenius has shown not to be the case, because the whole of the arsenic is deposited on passing the gas through a series of tubes, filled with loose cotton.

As in the process of Marsh, so it is in the method of Berzelius, absolutely necessary that the materials for the evolution of the hydrogen gas be free from arsenic. To exclude any possible intermixture of arseneted hydrogen with the hydrogen which serves for reduction, it has been recommended by Duflos and Hirsch to fill one half of the tube (a) Fig. 10 (the portion nearest to the gas-bottle), with loose cotton, soaked in a solution of corrosive sublimate, a salt which decomposes the arseneted hydrogen.

§ 51. Duflos and Hirsch have proposed another change in the method of Berzelius, namely, the substitution of the sulphide of arsenic by an arsenate.

The crude sulphide of arsenic is oxidized by means of nitric acid, the acid completely removed by evaporation, and the residue (to which a few drops of caustic potassa may be added), mixed with about six or eight parts of carbonized cream of tartar. The whole is made into a thick paste with a little water, and the mass shaped into small cylinders; these are then reduced, after perfect dessication, in hydrogen gas, as described in the preceding paragraph. I can assure, from my own experience, that by operating after this method, a pure mirror is obtained from a very minute quantity of arsenic, provided the destruction of the organic matters has been complete. It is always best to employ a perfectly pure sulphide of arsenic, prepared from the crude sulphide, in the manner described § 13. All that is true regarding the volatilization of the arsenic in the process of Berzelius, is also true in this process.

A more serious objection than the one just mentioned may be raised against the methods of Berzelius, and Duflos and Hirsch. It is this: that the compounds of antimony afford also a mirror, owing to the volatility of metallic antimony in a current of hydrogen gas; and it is on this account, more especially, that the method of Fresenius and Babo deserves the preference. The antimony-mirror may, however, be distinguished from that of arsenic by the reactions given in § 26. No spots of antimony can be obtained on porcelain during reduction; it is only on trying to drive the metal into the narrow part of the tube (an operation much more difficult to perform in this case than in that of arsenic), that these spots are formed; they are readily distin

guished from arsenic-spots by the tests given in § 27.

[§ 52. The process of H. Reinsch is founded on the observation that, from a dilute and acid solution of arsenious acid the arsenic is deposited, in the metallic state, on metallic copper, which is placed in the liquid. This deposition takes quickest place, when the solution is boiling and air has free access. The details of the process are as follows: the substances are cut into small fragments and mixed with hydrochloric acid, to the amount of about a tenth of the whole mixture, and more, if the subject of analysis is decayed or ammoniacal, so that there may be a decided excess of acid. The mixture is boiled gently for an hour, or until all soft solids are either dissolved or broken down into fine flakes or grains; and then strained through calico. The filtered fluid is again brought to the boiling point, and some bright copper leaf or fine copper gauze placed in it. The copper becomes covered immediately, or after some ten or fifteen minutes, with a thin, brittle, and steel-like coating of metallic arsenic. To prove that the deposit is really arsenic, the copper is removed from the liquid, dried with a gentle heat, and cut into small shreds. These shreds are heated in a glass-tube, narrowly drawn out at one end, when a sublimate of arsenious acid will be formed; this may be dissolved in caustic potassa, and the solution used for further experiments. Or the copper-leaf is heated to redness in a current of hydrogen gas when arseneted hydrogen is formed, which may be tested in the usual manner.

This method, though highly recommended by some

toxicologists, is open to many serious objections. On heating the copper with access of air, arsenite of copper may be formed, and some arseniuret of copper remain undecomposed, when, possibly, so minute a quantity of arsenious acid may sublime that it is insufficient for the tests. Arseneted hydrogen is not so easily formed under those circumstances, as usually stated, and brown spots may be deposited on metallic copper, in presence of hydrochloric acid and organic matters, even if no arsenic is present. If the arsenic occurs as sulphide, it escapes detection altogether, and if not arsenic, but another metal was the toxic substance, its presence is not indicated by this process. The last-mentioned objection is of great weight, the more so, as another poisonous metal—copper—is brought into the liquid under examination.]

[§ 53. An additional difficulty in the detection of arsenic in legal cases, occurs when the hydrate of sesquioxide of iron, which has been given as antidote, is not free from arsenic. In all cases, therefore, where this substance has been administered, it should be the first care of the analyst to subject a portion of it to Marsh's test. If this caution has been neglected, and the hydrate of iron is subsequently found to contain arsenic, the time and labor bestowed on the investigation is lost and valueless. If arsenic is found in the antidote, the contents of the stomach and the intestines have to be repeatedly washed with water, in order to effect as complete as possible a separation of the oxide of iron from other matters of less or greater density. If, during this process, particles of solid arsenious acid are found, which may have escaped the influence of the iron, the case offers

no further difficulties. But, if the analyst is not so fortunate to discover any arsenic in substance, it becomes very difficult and, frequently, impossible, to decide by chemical analysis, whether the arsenic detected in the body was introduced before, or only with the antidote, in other words, whether poisoning has been attempted or not. At all events, the liquid portion of the mass should be separated from the solids by filtration, and examined separately; if arsenic is found here, it is much more likely that the poison was administered alone, than that it was introduced with the antidote. A negative result, however, would by no means justify the conclusion that no poisoning has taken place, since the antidote may have fixed the whole of the arsenious acid. If any vomited matters, ejected before the administration of the antidote, are at the disposal of the analyst, an examination of these may lead to a satisfactory conclusion. But, if these also are wanting, there remains nothing to be done but to make a comparative quantitative analysis of the oxide of iron collected from the stomach and the oxide administered as antidote. From the difference in the amount of arsenic, found in either case, some conclusions may be drawn as to the nature of the case.

Without entering into the details of an investigation of this kind, which, in all probability, will but rarely be required, because it will rarely lead to a satisfactory result, I shall add a few remarks as to the best mode of procedure.

A portion of the oxide of iron found in the stomach, is repeatedly washed with water, then dried, and the weight ascertained.

The destruction of the adhering organic matter, and the conversion of the arsenious into arsenic acid, is effected by means of hydrochloric acid and chlorate of potassa, as described in § 9. The resulting liquid is mixed with tartaric acid in sufficient quantity to prevent the precipitation of sesquioxide of iron by ammonia, which is added in excess. To the ammoniacal solution a mixture of chloride of ammonium and sulphate of magnesia is added, when the whole of the arsenic acid is precipitated as arsenate of magnesia-ammonia ($2\,MgO.NH^4O$), AsO^5+HO; the precipitate is collected on a filter, washed with ammoniacal water, dried at 212°, and weighed. 100 parts of the salt correspond to 52.10 parts of arsenious acid.

A portion of the hydrate of iron, used as antidote, is treated in the same manner.]

§ 54. The following list, which contains the various apparatus and materials necessary for a legal analysis, may be found convenient for those who have not a well-furnished chemical laboratory at their disposal:

Large and small-sized porcelain-dishes (Berlin porcelain).

Small and very thin porcelain crucibles, to be used over a spirit-lamp.

Beaker-glasses, or Florence flasks, of various sizes.

Apparatus and materials for the evolution of sulphureted hydrogen, with washing bottle.

Several apparatus for the evolution of gas, of various sizes, for the tests of Marsh, and Fresenius and Babo.

Glass-tubes, especially the kind known as reduction-tubes of hard glass which is free from lead).

Spirit lamps with Argand burner.

Pure zinc, pure hydrochloric, sulphuric, and nitric acids, pure chlorate of potassa, nitrate and carbonate of soda, ammonia, etc. Strong

and freshly prepared sulphureted hydrogen water, sulphhydrate of ammonia, a newly-prepared alkaline solution of hypochlorite of soda (by passing chlorine gas into a solution of carbonate of soda).

A few practical remarks may conclude this important chapter.

The analyst should not allow any other operations to be carried on at the same time in his working-room; he should not lose sight of the various objects of examination during the time of his work, and lock them up on leaving the laboratory. The presence of other persons, while the investigation is carried on, is far from agreeable, and should be as much as possible avoided. It detracts the attention and does no mortal good. The apparatus to be used should be new, or, at least, cleaned with the greatest care. The last point, in particular, should be most conscientiously attended to, and mentioned in the written report.

CHAPTER II.

ON THE DETECTION OF ANTIMONY, TIN, MERCURY, COPPER, LEAD, AND ZINC.

§ 55. THE compounds of other metals are much more rarely made use of for willful murder, or self-destruction, than arsenious acid. In most cases of poisoning with such substances, the poison was taken by mistake or carelessness; and even this does not frequently occur, since they generally betray their presence by a peculiar metallic taste.

The number of metals treated of in this chapter may appear to some too small, to others too large; but other metals than those named will scarcely ever become the objects of a chemico-legal analysis. Nobody will raise any objections against copper, lead, and mercury. Food, cooked in copper vessels, sometimes takes up some of the metal; vinegar is often boiled purposely in vessels of copper for the manufacture of mixed pickles, to which it then imparts a fine, green color. Lead, or tin containing lead, when used for keeping or preparing articles of food, may produce poisonous effects; white lead and sugar of lead are articles of commerce, very accessible to the

public, and may serve for willful poisoning. Corrosive sublimate, red oxide of mercury, and white precipitate, all of which are violent poisons, find also application in the trades, and are of easy access. Antimony has been included in the number because cases of poisoning with tartar emetic have occurred; and zinc, on account of the extensive use which is at the present time made of vessels of zinc, and the frequent substitution of zinc-white for white lead as a paint; besides, there are cases on record of poisoning with white vitriol, which is easily mistaken for Epsom salt, or other salts. Tin is, perhaps, of all these metals, the one least likely to occur in chemico-legal investigations; it has been noticed on account of the general use which is made of its compounds in the operations of dyeing. It must be borne in mind that the attempt at poisoning, alone, may lead to chemico-legal analysis, and that these metals may become the objects of analysis with regard to medical police. To commit murder by poisoning with white vitriol must be considered next to impossible, but it may involve on the chemist to show that white vitriol has been administered by mistake, instead of Epsom salt, for example.

§ 56. It would be very erroneous to think that the presence of small quantities of the above-named metals is more easily ascertained than that of a small quantity of arsenic. There is, perhaps, no metal of which equally minute quantities can be detected with the same degree of certainty, as of arsenic. Even antimony, though greatly resembling arsenic in its properties, is no exception; it lacks that characteristic odor which arsenic emits on burning, and gives

no equally characteristic reaction with nitrate of silver. It is well known to every chemist that minute portions of mercury, tin, lead, and especially zinc, are very difficult of detection. Next to arsenic stands, perhaps, copper, since it is easily separated in the metallic state, even in small quantities.

If very small quantities of some of the metals under consideration have been detected, we are by no means justified to infer an attempt at poisoning. Traces of copper occur everywhere; I have attempted in vain to show its absolute absence anywhere; we eat it daily with our bread. Lead is also said to be very widely distributed in very minute quantities; its detection is attended with greater difficulties, hence its presence is not always so conclusively proved. The same may be the case with tin, which has been so frequently found by Berzelius in minerals, by treating them before the blowpipe in the reduction flame. Certain it is, that articles of food of acid reaction, when boiled in tinned vessels, take up some of the metal, without becoming thereby poisonous. Antimony and mercury do not, perhaps, so generally occur, but it should always be remembered that their compounds are extensively used as medicines, and it is said to be an authenticated fact that metallic mercury is sometimes found in the body of persons who have used for some time mercurials as a medicine.

§ 57. It might appear from the preceding remarks that it would be very difficult to decide the question whether poisoning has taken place or not. But, I think, the difficulty is not so great as it appears at first sight. There can, in my opinion, hardly ever

arise any doubt as to whether, for instance, the copper found in articles of food, or the contents of the stomach, is the minute quantity which everywhere occurs, or whether it originated from copper vessels, or is intentionally mixed with the food. A practised and well-qualified expert will certainly be able to decide the point, while an inexperienced and not sufficiently qualified person does not find the minute, and as it were normal, quantity of copper at all. The same remark is still more applicable in regard to lead, tin, &c. In cases of willful murder, and still more so of suicide, the quantity of the poison administered is almost invariably much larger than necessary—a circumstance which not unfrequently saves the life of the person. It is usually only in cases of accidental poisoning that the quantity of the poisonous metal to be detected is very small; so ex. gr. in poisoning with food, which has been boiled in vessels of copper, zinc, etc.

In most cases, and even in those of willful murder, a remnant of the substance which served for poisoning will be at the disposal of the analyst. This occurs still more frequently in cases of suicide, and almost invariably if the toxic principle was taken by mistake, or carelessness, there being no reason for removing or hiding the rest of the poison. But, for reasons already stated, the majority of cases of poisoning with the metals in question will be of the latter description.

§ 58. What substances may become the objects of analysis it is utterly impossible to predict; contents, vomited matters, articles of food, commercial and chemical preparations, etc., may become objects of

investigation. We shall pursue here the same way as in the case of arsenic, and assume the case to be of the most complicated kind, where the metallic poison is mixed with organic matters, as it will be when vomited matter, contents, etc., are to be examined. The method for cases of a less complex nature is then easily derived from this.

In embracing the metals to be treated of in this chapter under one head it was not meant to intimate their simultaneous occurrence, but it was done simply to avoid frequent repetitions, and because such an arrangement offers great advantages for cases where there is no indication whatever as to the nature of the poison. The remark has been made on several occasions in the preceding chapter, that such and such a method for the detection of arsenic could not be recommended, because it did not lead at the same time to the detection of other poisonous metals. To the method indicated as the best, this deficiency does not apply; it leads to the detection of all the above-named metals, if the analyst chooses to take account of them, that is to say, if he looks for them at the proper stage in the course of the investigation. Up to a certain point, the method for the detection of the metals in question coincides with the one given for the detection of arsenic, and, unless we are convinced of the absence of the latter, due attention should be paid to its possible occurrence.

§ 59. To make random experiments for the presence of one or the other of the metals will, as a general thing, be a useless task, because the soluble metallic compounds are almost invariably converted into insoluble ones when organic matters are pre-

sent. Copper may possibly betray its presence by a greenish color, and by the blue coloration produced by ammonia. It is, therefore, best to subject the substances under examination directly to the treatment with hydrochloric acid and chlorate of potassa, in exactly the same manner as described for arsenic in § 9. The free chlorine is then removed by a continued gentle heat, the residue diluted with water and allowed to cool; the mass is then filtered, the residue well washed with water, and put aside for further examination, if it should appear desirable.

The filtrate, provided the operation to have been carefully conducted, is a perfectly limpid liquid, of a yellowish color, in which, without further preparation, the presence of some metals, if not occurring in too small a quantity, may be satisfactorily detected by the proper reagents.

A portion of the liquid is mixed with ammonia in excess; if it becomes blue, the presence of copper is indicated. The color is most clearly seen on holding the test-tube against a sheet of white paper. The blue color assumes a greenish tinge in proportion as the yellow color of the liquid was deeper.

Ferrocyanide of potassium, added to another portion of the filtrate, produces a red precipitate, or merely a red color of the liquid, even in presence of a very small quantity of copper; the presence of iron makes the reaction indistinct.

The presence of lead may be demonstrated by sulphuric acid. To a portion of the filtrate some rectified, concentrated (or better, slightly diluted) sulphuric acid is added, drop by drop; a white precipitate, or turbidness, indicates lead.

In a similar manner, the presence of mercury may be shown by protochloride of tin, which causes a white turbidness, and by metallic copper, which becomes amalgamated (see § 64).

§ 60. Whether, by these reagents, indications are obtained, or not, the filtrate is now treated with sulphureted hydrogen, in the manner described § 10. The metals under consideration, with the exception of zinc, are precipitated as sulphides, provided the liquid was sufficiently dilute. The liquid, saturated with the gas, is allowed to rest at least twenty-four hours, to effect a complete precipitation and separation of the metallic sulphides.

We have next to take the color of the precipitate into consideration. If the precipitate consists of sulphide of lead, sulphide of copper, or sulphide of mercury, the color is dark; it is light, if the precipitate consists of sulphide of antimony, or sulphide of tin, or if none of the metals in question are present (compare § 10). The sulphides of lead and mercury are of a pure black color; they are pulverulent, and settle readily to the bottom. The sulphide of copper is blackish-brown, hydrated, and settles down less easily; the liquid retains, for a considerable time, a brown coloration. The sulphide of antimony is not precipitated with its characteristic orange-red, but with an impure yellow color. In presence of lead, the precipitate is, at first, usually of a cinnabar-red color (chlorosulphide), which becomes gradually black (pure sulphide). If, from this and previous reactions, the presence of lead has been inferred, the residue from the treatment with hydrochloric acid and chlorate of potassa is once more washed with hot water,

to dissolve any chloride of lead which it might contain. This residue may subsequently be examined for the presence of sulphate of lead.

§ 61. The precipitate must now be collected. Let us suppose it to be of a dark color. It will be found very convenient to avoid, altogether, the use of filtering-paper, and, with the necessary precaution, it may be avoided. The sulphides of lead and mercury are deposited in a pulverulent state, and it is a very easy matter to pour off the supernatant liquid, and to wash the precipitate by repeated additions of water; glasses of conical shape are advantageously employed in this operation. The precipitate is finally transferred from the glass into a porcelain dish, and dried at a moderately warm spot. The sulphide is thus obtained in a very pure condition. The washings are all united in a large beaker-glass, not to lose traces of the precipitate which might have been poured off with the liquids. The sulphide of copper is not deposited in an equally compact state; on pouring off the supernatant liquid, small, flaky particles of the precipitate are very apt to pass off with it. But, with patience, which conquers many difficulties, also this one may be overcome, and the washing of the precipitate be effected by decantation.

The precipitate may, also, very conveniently be collected in a funnel, into the barrel of which a small plug of fibrous asbestos is loosely fitted. A few experiments will very soon show the necessity of having the plug but loosely fitting, and not pressed into the barrel, to admit of ready filtration. A few drops of water poured on the plug, and which serve at the same time to moisten the asbestos, show whether it

is of the proper condition. The liquid is removed from the precipitate, as much as possible, by decantation, and the residue stirred up and poured into the funnel. Filtration proceeds but slowly, but the solid matter collects very well in the lower portion of the funnel, and does not, to any extent, adhere to the glass. It is then very easily washed. The moist precipitate is removed from the funnel by means of a small spatula of platinum, and placed into a porcelain dish, ready for dessication.

To the precipitate contained in the dish, some moderately concentrate nitric acid is added, and a gentle heat applied.

§ 62. *Copper.*—If the precipitate consisted of sulphide of copper, nitric acid effects complete solution, and the resulting liquid is of a blue color. The liquid is mixed with a little sulphuric acid (to remove the nitric acid), and evaporated till nearly dry; a bluish mass is obtained. If, on evaporation, the mass does assume a dark color, owing to the presence of organic matters, a little chlorate of potassa is added. A similar addition, together with a corresponding amount of sulphuric acid, has to be made, if the precipitate has been collected on a filter, and then been treated with nitric acid. The residue here, as in the other case, is of a pure, greenish-blue color. The residue is then dissolved in water. In the resulting solution, the presence of the copper is demonstrated by the usual reagents. Ammonia, added in excess, imparts to the liquid a deep blue color. Ferrocyanide of potassium causes a brownish-red coloration, or brownish-red precipitate. A piece of

bright, metallic iron—a knife-blade, or a knitting-needle—becomes coated with metallic copper.

If a quantitative determination of the copper is desired, the solution is weighed, and a small weighed portion of it used for the qualitative tests; the remaining portion is heated to ebullition, and the oxide of copper precipitated by caustic soda; the precipitate is collected on a filter, washed, dried, and ignited in a porcelain crucible until the filter is completely consumed. It is then weighed and, from the weight obtained, the whole amount of oxide found by calculation. Or, the whole of the liquid is used for this precipitation, and the weighed oxide afterwards dissolved in nitric acid and sulphuric acid; the resulting liquid is then used for the qualitative tests. After having precipitated with caustic soda, the liquid usually retains a blue color, even if the original precipitate of sulphide of copper was not collected on a filter, and if chlorate of potassa was used for the destruction of the organic matters. In this case, a little grape-sugar (honey) is added, when the last trace of copper is precipitated as red suboxide; by ignition it passes into protoxide.

§ 63. *Lead.*—If the precipitate, caused by sulphureted hydrogen, consisted of sulphide of lead, it becomes decolorized by the action of nitric acid. Some sulphuric acid (and, if necessary, some chlorate of potassa) is added, and the whole evaporated to dryness. On adding water to the residue, a white powder, sulphate of lead, remains undissolved.

The contents of the dish are next washed into a conical glass; the powder is allowed to settle, and

repeatedly washed with water. The decanted liquids are united in a large beaker, to recover any washed-off particles. With the necessary patience and circumspection, the whole of the sulphate of lead may thus be collected, without the use of a filter. The pulverulent salt tends to adhere to the sides of the vessel; but, by carefully stirring the liquid above the precipitate, the greater part is readily brought down, and the remaining portion usually adheres so fast to the glass, that it does not pass out with the liquid.

The decomposition of the sulphate may now be effected in the same vessel. A solution of carbonate of soda is poured on the precipitate, and left in contact with it for several hours, the precipitate, during this time, being frequently stirred up. The limpid liquid is then poured off, and the operation repeated with a fresh solution of carbonate of soda. Carbonate of lead is formed, which is several times washed with water. The decanted liquids are, as before, united in a large beaker.

According to H. Rose, solutions of neutral alkaline carbonates exercise a slight solvent action on carbonate of lead; for this reason, it might be better to substitute the carbonate of soda by the bicarbonate of soda or ammonia. A liquid which is turbid from finely suspended particles of sulphate of lead, appears much less so after addition of carbonate of soda.

A little water is then poured on the carbonate of lead, and some nitric acid added, drop by drop. It dissolves completely to a perfectly limpid liquid, in which the presence of the metal may be shown by means of the usual reagents. Chromate of potassa

produces a yellow precipitate of chromate of lead. Iodide of potassium throws down yellow iodide of lead; the precipitate dissolves on boiling the liquid, and separates, on cooling, in gold-like scales. Sulphuric acid precipitates white pulverulent sulphate of lead, etc.

If the lead is to be quantitatively determined, the sulphate of lead, collected in the conical glass, may be washed into a weighed porcelain dish, dried, and weighed. It is, then, again softened with water, and decomposed by a solution of carbonate of soda, as above explained.

Although filtration may very well be avoided in operating after the method just described, there is, of course, no objection to collect the sulphate as well as the carbonate of lead on a filter. If the sulphate is collected on a weighed filter, it may, after washing and drying, be weighed with the filter, and thus quantitatively determined. It is, then, together with the filter, if this cannot be conveniently removed, digested with a solution of carbonate of soda, washed, and the carbonate dissolved in dilute nitric acid.

§ 64. *Mercury.*—If the precipitate, produced by sulphureted hydrogen, consisted of sulphide of mercury, it suffers no change by the action of nitric acid; it remains black. (If the precipitate was not thoroughly washed and, thereby, freed from any chloride, solution may take place.) Hydrochloric acid is then added, heat applied to the mixture, and the resulting liquid evaporated till nearly dry. The residue is dissolved in water (if, on addition of water,

some yellow protosulphate of mercury should remain undissolved, a few drops of hydrochloric acid must be added), and the liquid tested with the proper reagents. A drop of a freshly prepared solution of protochloride of tin (by dissolving tin in hydrochloric acid), produces a white turbidness, or a white precipitate of subchloride of mercury; on addition of a larger quantity of the reagent, the white color passes into grey, owing to the reduced mercury. A drop of the liquid is placed on a piece of bright copper-foil, or copper coin (cleaned with nitric acid), and the copper touched, through the liquid, with a zinc rod; metallic mercury is precipitated; the liquid is carefully removed by means of blotting-paper, and the spot rubbed with the finger, or with a piece of soft wood, when it assumes a white appearance. These reactions are conclusive; to obtain the well-known indications with potassa, ammonia, and iodide of potassium, it requires the presence of a considerable quantity of mercury.

The presence of mercury being thus demonstrated, the whole of the liquid is transferred into a small Florence flask, and, aided by a gentle heat, precipitated with protochloride of tin. The contents of the test-tube, which served for the qualitative test with protochloride of tin, are added to this liquid. The reduction being completed, the liquid is carefully poured off, and the metallic mercury washed into a small, weighed porcelain dish. It is washed with water, the last drops of adhering liquid removed by blotting-paper, and dried by exposure to air, or by application of a very gentle heat. By gently heating the finely divided mercury with a little hydro-

chloric acid, it usually unites to larger globules. The dried mercury is weighed with the dish.

To prevent any loss of the metal, the washings are united in a glass of conical shape. The weight of the mercury having been ascertained, a few additional experiments may be performed. By rubbing the finely divided metal with the finger, it unites to larger globules; by rubbing a little of it on a piece of copper, the copper becomes amalgamated; by placing a few globules in a glass tube and applying heat, the characteristic coating of metallic mercury is produced, which, by friction with a piece of wood, forms bright metallic globules.

§ 65. *Antimony—Tin.*—If the precipitate, produced by sulphureted hydrogen, is of a light color, it may consist of sulphide of antimony, or sulphide of tin (or sulphide of arsenic). It is collected on a filter, washed with water, and treated with sulphide of ammonium, in order to dissolve it. The filter, for this operation, may either remain in the funnel—and the solution is promoted by stirring the precipitate with a feather, or by using the washing-bottle—or it is placed in a porcelain dish, unfolded, sulphide of ammonium poured on it, and the solution filtered.

The solution is evaporated to dryness in a porcelain dish, the residue moistened with concentrated nitric acid, and the acid removed by gentle heat. The residue is mixed with pure carbonate of soda and some nitrate of soda, and the mixture heated to fusion in a porcelain crucible (v. § 13). The quantities of the carbonate and nitrate of soda should be proportional to the amount of residue, and the cru-

cible not larger than necessary. The mixing of the residue with the pulverized soda-salts may be effected by means of a small platinum spatula, or by rubbing the sides of the dish with the pulverized salts by means of a rounded piece of cork, or the finger.

The fused, colorless mass is, after cooling, treated with water, and a gentle heat applied. The contents of the crucible are then transferred into a test-tube. If a white precipitate is deposited in the tube, the original precipitate, produced by sulphureted hydrogen, may have been either sulphide of antimony, or sulphide of tin. If it was the former, the deposit is antimonate of soda; if it was sulphide of tin, the deposit is binoxide of tin, and, in this case, a small quantity of the tin will be found in the liquid in the shape of stannate of soda.

If the fused mass dissolves completely in water, the absence of antimony is proved. The precipitate caused by sulphureted hydrogen either contained no metallic sulphide, or it consisted of sulphide of arsenic, or it contained only a very minute quantity of sulphide of tin, in which case the whole of the binoxide of tin may have entered into solution as stannate of soda.

§ 66. We shall first consider the case where only partial solution has been effected. If the analyst has sufficient time and patience at his disposal, the solution is allowed to rest until the undissolved matter has settled; the liquid is poured off, and the precipitate washed with water. Or the undissolved portion is collected on a very small filter—which has previously been treated with dilute acid, and the acid

been removed by washing with water—and the filtered liquid put aside for further examination.

It has now to be ascertained whether the undissolved matter is antimonate of soda, or binoxide of tin. To this end, it is placed in a small porcelain crucible (if it was collected on a filter, the filter must first be carefully and completely incinerated), and some cyanide of potassium, in small pieces, added. Heat is applied until the salt has entered into fusion. The reduction of metallic antimony from the antimonate of soda, or of metallic tin from the binoxide takes place very readily. The flux blackens during the process, and, if the amount of tin is not very small, bright metallic globules make their appearance. After cooling, the contents of the crucible are softened with water, and washed into a porcelain dish (if any particles of reduced metal should adhere to the sides of the crucible, they may be removed with the point of a knife); the metal readily collects at the bottom; it is washed, dried, and weighed. The washings are collected, as usual, in a large beaker, to prevent any loss of metal.

The metal is now gently heated with some hydrochloric acid. If it is tin, the small particles dissolve immediately, and afford a liquid in which the presence of this metal may be very satisfactorily demonstrated. A few drops of the liquid are poured into a dilute solution of protochloride of mercury; a white precipitate is produced, which, on addition of a larger quantity of the solution of tin, becomes grey, owing to the reduction of mercury. The very smallest trace of tin may be thus detected; even the

grey coating which remains adhering to the sides of the crucible, after being dissolved in a few drops of hydrochloric acid, may thus be recognized as tin. It is evident that, if the amount of tin is very small, only the white precipitate is produced. A neutral solution of terchloride of gold assumes, on addition of the solution of tin, a dark color, owing to the reduction of the gold; this test is much less delicate than the preceding. A few drops of the solution are placed in a test-tube, and mixed with sulphureted hydrogen water; a brown precipitate of protosulphide of tin is thrown down; but if the solution is previously heated with a few drops of nitric acid (to convert the protochloride into the bichloride of tin), the precipitate caused by sulphureted hydrogen is yellow; it is the bisulphide of tin. The larger globules of the metal are readily flattened into thin scales of bright metallic lustre.

§ 67. If these experiments give a negative result, the absence of tin is proved. The metal is then heated with some hydrochloric acid, to which a few drops of nitric acid are added. A violent reaction takes place; chloride of antimony is formed. The solution is gently heated to remove the nitric acid, and the residue mixed with water. If the quantity of antimony is not too small, a white turbidness is produced by the addition of water, owing to the formation of a basic chloride of antimony (pulvis algarothi.) The turbidness disappears on addition of hydrochloric acid, and the limpid solution affords with sulphureted hydrogen water the characteristic orange-red precipitate of sulphide of antimony. This reaction makes all other tests superfluous; if, however, it should appear

desirable to corroborate the result by another experiment, the solution may be introduced into Marsh's apparatus, and spots of antimony on porcelain be produced. The spots are then examined as described, § 26–30.

§ 68. If the fused mass has dissolved completely (v. § 65), the solution is mixed with some nitric acid, which is added drop by drop. In presence of stannate of soda, white flakes of binoxide of tin are now precipitated, which again dissolve on addition of more acid. In this case the liquid is neutralized with carbonate of ammonia, left to rest for a short time, and the binoxide of tin collected on a small filter; it is then reduced by means of cyanide of potassium as above described. If the fused mass, on being treated with water, left a residue, and the residue was subsequently recognized as oxide of tin, then the solution is treated in exactly the same manner. Having thus removed the tin the liquid may be mixed with some sulphuric acid, evaporated to dryness, and the residue tested for arsenic (v. §13, etc.)

The method just described for the treatment of the precipitate produced by sulphureted hydrogen, leads easily and safely to the detection of antimony and tin, and does not interfere with a subsequent examination for arsenic. It is only for the sake of completeness, therefore, that another process, which also gives very satisfactory results, will be described.

§ 69. The precipitate is dissolved in sulph-hydrate of ammonia, the solution acidulated with hydrochloric acid to reprecipitate the sulphide, and the precipitate collected on a small filter, or in a funnel plugged with asbestos. It is then washed with water,

placed in a porcelain dish, and heated with concentrated hydrochloric acid. If the precipitate consisted of sulphide of tin or sulphide of antimony it will dissolve. The solution is filtered through paper, the residue washed with water, and the filtrate, together with the washings, concentrated by evaporation. The concentrated liquid, freed from its excess of acid by the preceding operation, is again diluted with water; a small rod of pure metallic zinc is then placed in the solution. Tin and antimony are precipitated in the metallic state, forming a black coating on the zinc. After about twelve hours the coating is washed off or scraped off from the zinc, the latter removed from the liquid, and the precipitated metals treated in the same manner as the metals obtained by the reduction with cyanide of potassium (v. § 66.) The resulting solution is tested as above (§ 66–67.)

If neither antimony nor tin has been found, the residue from the treatment with hydrochloric acid has to be tested for arsenic. For this purpose it is treated with ammonia, the solution evaporated to dryness, and the residue operated upon as described, §12, etc.

It has to be borne in mind that the object of a chemico-legal investigation is almost invariably the detection of a certain poison (in the case under consideration, of a metal), but not the separation of different metals; hence the examination consists in testing for the different metals. But even if several metals should occur simultaneously, the mode of procedure which we have recommended will enable the analyst to obtain the most satisfactory results.

§ 70. *Zinc.*—There remains to be considered the

liquid filtered off from the precipitate which was caused by sulphureted hydrogen. If the substances under examination contained zinc, it will be found in this liquid. It is made slightly alkaline by addition of ammonia, and then mixed with sulph-hydrate of ammonia. In presence of zinc a precipitate of a dirty greenish-grey color is thrown down. The precipitate is allowed to settle, and then dilute acetic acid added until the liquid shows an acid reaction; the whole is well stirred up and left to rest for some time. The precipitate becomes gradually of a lighter color, owing to the entering into solution of the sulphide of iron, which, together with the sulphide of zinc, was precipitated by the sulph-hydrate of ammonia. Phosphates of the alkaline earths, if present, are also dissolved. The precipitate is collected, washed with water, dried, and calcined (with the filter) in a porcelain crucible. The calcined mass is dissolved in sulphuric acid, with addition of some hydrochloric or nitric acid, the solution freed from the excess of acid by evaporation, and diluted with water. The dilute liquid, which is a watery solution of sulphate of zinc, is filtered, and the filtrate tested for zinc with the proper reagents. A portion of the liquid is mixed with concentrated sulphureted hydrogen water; no precipitate is produced; but on adding a solution of acetate of soda, sulphide of zinc is thrown down in the shape of a white flocculent precipitate. Sometimes a precipitate is produced by sulphureted hydrogen alone; but this is only the case when the excess of sulphuric acid was *entirely* removed by evaporation. Caustic soda precipitates, on careful addition, white hydrate of zinc, readily

soluble in an excess of the reagent. In this solution sulphureted hydrogen causes a white precipitate of sulphide of zinc. Carbonate of soda precipitates on boiling carbonate of zinc. The whole of the solution may be treated in this manner, the precipitate be collected, ignited, and weighed. The carbonate, by ignition, is converted into oxide.

§ 71. If the examination has led to the detection of a fixed metal, the residue from the treatment of the substances under examination with chlorate of potassa and hydrochloric acid may be dried, carbonized, and incinerated, and the metal be quantitatively determined. In this residue chloride of silver will be found in case a salt of silver was administered. By treating the residue with ammonia the chloride of silver is dissolved, and may be precipitated from the solution by an addition of nitric acid. The whole amount of silver cannot thus be ascertained, since a certain portion of the chloride will have entered into the solution which is filtered off from the original residue, owing to the presence of the large quantity of chloride of potassium.

CHAPTER III.

ON THE DETECTION OF HYDROCYANIC ACID.

§ 72. HYDROCYANIC acid belongs to the class of narcotic poisons. Though the pure acid is not easily accessible to the public at large, still cases of accidental and willful poisoning with the medicinal acid, with cyanogen compounds, and with the various essential oils and distilled waters, into the constitution of which prussic acid enters as a constituent, are of frequent occurrence. Whether the pure acid, or one of its components, has been administered, the object of the analyst's investigation is the detection of hydrocyanic acid, this substance being the toxic principle; what the other components of the compound are, it is, in most cases, immaterial to know. The method to be pursued is the same for the pure acid and its compounds.

§ 73. If the quantity of hydrocyanic acid is not too small, and no other strongly odorous substances are present, its presence is usually betrayed by its characteristic odor of bitter almonds; particular attention should, therefore, be paid to this point, at the *post-mortem* examination.

[This, however, is by no means a constant phenomenon.—(*Pelikan*).

According to the experiments of Pelikan,* this acid may always be detected in the contents of the stomach, by the processes detailed below (§ 74), whenever the peculiar odor is distinctly perceptible. But, if the odor was wanting, or but indistinctly perceived, he never obtained indications of its presence by chemical reagents. The peculiar odor must, therefore, be considered as one of the most important indications of the presence of this poison, though not the safest, or most conclusive.

Here, as in all cases of medico-legal analysis, it is not on one observation alone that a judgment should be formed, but the opinion must be based on the agreement of all the various tests.

To detect the presence of hydrocyanic acid in substances of various kinds, ex. gr. in food, contents of the stomach, we proceed as follows:]

§ 74. The substances, if solid, are cut into small pieces or shreds, and made into a thin paste with distilled water. If the mass does not show acid reaction, it is slightly acidulated with sulphuric acid, introduced into a retort, the latter placed over a water-bath, and distilled until several grammes of liquid have passed into the receiver.

In the distillate the presence of hydrocyanic acid may be shown very conclusively by the application of reagents, and, if the quantity is not too small, be recognized by the smell.

* Zur Toxikologie der Cyan Metalle, von Prof. Eugen Pelikan, in Vierteljahrschrift für die pract. Heilkunde. Prag. 1856.

§ 75. A part of the distillate is introduced into a small test-tube, and a few drops of caustic potassa, and afterwards a few drops of a solution of green vitriol added; the mixture is stirred with a glass-rod, until the precipitate assumes a greenish color. Ferrocyanide of potassium is formed. The liquid must have an alkaline reaction. Hydrochloric acid is now added, drop by drop, to dissolve the excess of the black oxide of iron; an addition of some sesqui-chloride of iron by means of a glass rod, will sometimes make the reaction more distinct, but is not indispensable, since there is usually sufficient of the sesqui-oxide formed by the action of the air. If the distillate contained any hydrocyanic acid, there remains a blue residue of Prussian blue undissolved; but if the quantity is very small, the liquid assumes only a blue, or greenish blue color, and, after some time, a blue precipitate is deposited. This reaction is so delicate and characteristic, that it makes every other test almost superfluous.*

[It is very important that the liquid have an acid reaction, because many organic substances produce, with the salts of iron, a bluish-colored liquid, or even a bluish precipitate, but these disappear on addition of an acid.]

§ 76. To another portion of the distillate, a few drops of sulphide of ammonium are added, and the mixture heated, very gently, in a small capsule, until

* I cannot recommend the method of heating the liquid containing the hydrocyanic acid with caustic potassa and green vitriol, for the purpose of facilitating the formation of ferrocyanide of potassium, because the precipitate of black oxide becomes very compact, and does not easily dissolve in hydrochloric acid.

it has become colorless. If necessary, the evaporation must be carried to dryness, and the residue dissolved in a little water. The colorless liquid is then feebly acidulated with hydrochloric acid, and a drop of sesqui-chloride of iron added; the liquid assumes a blood red color if the distillate contained hydrocyanic acid (*Liebig*). This test is founded on the observation that hydrocyanic acid forms with sulphide of ammonium, sulphocyanide of ammonium, which produces, with the sesqui-salts of iron, the peculiar blood red color. This reaction is also very delicate, and possesses the advantage of admitting of a concentration of the liquid under examination by heat.

[In making this test, particular care should be taken to remove the excess of sulphide of ammonium, as indicated, by evaporation, and not to add the salt of iron until the liquid has become quite colorless; for, if this precaution be not observed, a black precipitate of sulphide of iron is thrown down, which interferes with the reaction. Small quantities of free acid do not change the blood-red color of the liquid, but additions of larger quantities make it paler. Nitric acid destroys the coloration; ammonia decolorizes the liquid immediately, and throws down the hydrate of the sesqui-oxide of iron. Reducing substances, ex. gr. sulphureted hydrogen, protochloride of tin, metallic iron, cause the disappearance of the color, by converting the sesqui-oxide of iron into the protoxide.

Before subjecting the distillate to this test, it is absolutely necessary to convince one's self of the absence of acetic, formic, and meconic acids, which also possess the property of imparting a red color to

the sesqui-salts of iron. It is, therefore, advisable to test the distillate, previous to its treatment with sulphide of ammonium, with a drop of sesqui-chloride of iron; if a red color is produced, this reaction has either to be abandoned, or the above-named acids have to be removed—a problem of considerable difficulty.

The delicacy of the test is very great. It gives a distinct reaction, when the mixture of a proto and sesqui-salt of iron produces only a faint blue coloration, which is by no means so characteristic as the blood-red color produced by this test. To detect, after this method, the presence of a very small quantity of hydrocyanic acid, the substance is placed in a watch-crystal, and another watch-crystal, at the bottom of which a drop of sulphide of ammonium has been placed, inverted over it. A very gentle heat is applied to the lower glass, for about ten or fifteen minutes. The upper glass is then removed, the liquid which it contains evaporated to dryness at a very gentle heat, and the residue moistened with some sesquioxide of iron. It must be borne in mind that the reaction is produced only by *free* hydrocyanic acid; compounds ex. gr. cyanide of silver, have previously to be moistened with a drop of hydrochloric acid.]

§ 77. Lassaigne recommends to add to the distillate a few drops of caustic potassa, and, immediately afterwards, a few drops of a solution of sulphate of copper; the mixture is then feebly acidulated with hydrochloric acid. If the distillate contained hydrocyanic acid, a greenish-yellow (protocyanide of copper), or white (subcyanide of copper) precipitate

remains undissolved; but, if no hydrocyanic acid was present, the precipitate, consisting of pure hydrate of oxide of copper, is wholly re-dissolved. According to Berzelius, a similar reaction is produced by hydriodic acid.

[A person not experienced in chemical manipulations is liable to obtain wrong indications with this reagent. Too little potassa, or too much sulphate of copper, prevent the formation of the precipitate; the addition of too much hydrochloric acid, on the other hand, causes the re-solution of the whole precipitate, even if hydrocyanic acid was present.—*Schneider.*]

[§ 78. Another portion of the distillate is tested with a few drops of nitrate of silver. This reagent produces in acid, or neutral liquids containing hydrocyanic acid, a white, curdy precipitate, which is soluble in ammonia; from the ammoniacal solution the cyanide of silver is re-precipitated by an excess of nitric acid. This white precipitate is not characteristic of hydrocyanic acid. The same reaction is produced by hydrochloric, hydriodic, hydrobromic, carbonic, phosphoric acids, and several other substances. It is, therefore, necessary to prove, by other experiments, that the precipitate really contains cyanide of silver. For this purpose, the precipitate is *thoroughly* dried, and the dry mass introduced into a small test-tube, closed at one end, and narrowly drawn out at the other; on applying heat, which may be raised to redness, cyanogen gas escapes, which, when kindled, burns with a purple flame. Orfila states that one grain of cyanide of silver, treated in this manner, evolves sufficient gas to show the red flame very distinctly.

To get rid of hydrochloric acid and other substances which interfere with this reaction, Otto recommends to rectify a portion of the original distillate by re-distillation over powdered borax or carbonate of lime. Hydrochloric acid, etc., are retained by the borax, or the carbonate of lime, while hydrocyanic acid passes over, and may be detected in the distillate by precipitation with nitrate of silver.]

§ 79. It is sometimes very convenient to fix a small quantity of hydrocyanic acid, which may occur in a distillate, so as to prevent its volatilization, and form a compound which may afterwards be easily tested with reagents. This is effected by agitating the distillate with some red oxide of mercury; a solution of cyanide of mercury is obtained which may be evaporated without suffering decomposition. If hydrochloric acid was present, protochloride of mercury (corrosive sublimate), is formed at the same time, and, in this case, ammonia causes a white precipitate, owing to the decomposition of the chloride while the cyanide remains unchanged, and nitrate of silver throws down chloride of silver, leaving the cyanide unaffected.

[§ 80. Instead of simply condensing the vapors in a receiver as in the process above (§ 74) given, Orfila connects the retort with a delivery-tube, bent at a right angle, the vertical leg of which is about three and a half feet long, and dips into another tube of about the same length, which is filled to about two-thirds with a solution of nitrate of silver. The retort is heated in a sand-bath, and the liquid kept in ebullition for about an hour. The precipitate which is

formed in the silver solution is allowed to settle to the bottom, the supernatant liquid is poured off, and some pure, cold nitric acid added to the precipitate; this dissolves the carbonate of silver. The cyanide is then collected on a filter, dried at 212° (weighed, if it is thought desirable), and tested by heating in a glass-tube (v. § 78). A portion of the dried precipitate may be tested in the following manner: it is mixed with about half its weight of chloride of sodium, a little water added, and the whole boiled for a few minutes; chloride of silver and cyanide of sodium are formed, which latter may be tested with green vitriol (§ 75). An excess of chloride of sodium has to be avoided, lest the cyanide of silver enter undecomposed into solution, and make the reaction with green vitriol indistinct.]

[§ 81. Whether these operations have given a positive or a negative result, it is always advisable to subject the contents of the retort to a further treatment. The mass, if too pasty to admit of filtration, is stirred with some distilled water, filtered, and the filtrate precipitated with nitrate of silver. The precipitate, after having been well washed with distilled water, is treated with dilute nitric acid in the cold; the carbonate, phosphate, etc., are dissolved, and the residue consists essentally of chloride and cyanide of silver. It is tested for the presence of the latter by the processes given above (§ 78).]

§ 82. If by the method above described (§ 74), we obtain a distillate in which, by the use of proper reagents, the presence of hydrocyanic acid can be demonstrated, this can by no means be considered as a proof for the presence of hydrocyanic acid or,

respectively, of cyanide of potassium,* unless we have previously shown the absence of ferrocyanide of potassium.* Ferrocyanide of potassium, a salt which does not possess poisonous properties, also yields on distillation a liquid which contains hydrocyanic acid, even if the contents of the retort are but very slightly acid, or in presence of even a very weak acid; and this will occur even if the distillation is effected at the lowest possible temperature. Apparently no hydrocyanic acid is given off at first on distilling over a water-bath a mass containing ferrocyanide of potassium; after awhile, however, decomposition takes place, and hydrocyanic acid is evolved. Hence it is necessary to test the substances under examination for the presence of ferrocyanide

* [Of poisonous cyanides the author has only considered the cyanide of potassium, and of not poisonous, the ferrocyanide of potassium. These two compounds may be considered as the types of the two great classes of cyanogen-compounds, the one comprising the poisonous, the other the not poisonous ones.

To the first class—the poisonous cyanogen-compounds—belong all soluble simple cyanides of the constitution, M Cy, and all double cyanides which form no acids. Among the simple cyanides only those of the alkalies and earths, and the cyanides of mercury, and cadmium are soluble in water. Of the insoluble ones, the cyanides of zinc, copper, lead, and silver are under the influence of the living body so decomposed that hydrocyanic acid is set free; they are, therefore, also poisonous. Of the double cyanides of this class, those soluble in water exercise a more powerful poisonous action than those insoluble in water; both kinds are decomposed by dilute acids, especially by hydrochloric acid, and hydrocyanic acid is set free.

The second class—the non-poisonous cyanogen-compounds—comprises all insoluble double-cyanides which show acid properties, and some few of the soluble ones. These are very stable compounds, and decomposable only by powerful acids; they are not acted upon by dilute acids.—*Pelikan.*]

of potassium before subjecting them to distillation. To this end a portion of the original substance is, if necessary, mixed with water, thrown on a filter, the filtrate acidulated with hydrochloric acid, and a drop of sesquichloride of iron added. The formation of a precipitate of Prussian blue indicates the presence of ferrocyanide of potassium.

§ 83. The question now arises, how to operate when hydrocyanic acid, or cyanide of potassium, and ferrocyanide of potassium occur simultaneously? *i. e.* how can we show in this case the presence of hydrocyanic acid or cyanide of potassium? To add an excess of carbonate of soda to the mass before subjecting it to distillation, does not lead to a satisfactory result; it is true that the decomposition of the ferrocyanide of potassium is thereby prevented, but the hydrocyanic acid becomes at the same time fixed, so that at the beginning of the operation not a trace of it is obtained, and even at a later period only traces of the acid, resulting from the decomposition of the cyanide of sodium, pass into the receiver. If a solution of carbonate of soda, to which some hydrocyanic acid is added, is heated, carbonic acid escapes, showing that the acid properties of hydrocyanic acid are not so weak as is generally believed.

According to experiments which Mr. Von Pöllnitz made in my laboratory, the best way to follow in this case is this: The mass containing ferrocyanide of potassium, and, eventually, hydrocyanic acid, is mixed with a solution of sesquichloride of iron, when the ferrocyanide of potassium is converted into Prussian blue; carbonate of soda is then added, until the mass exhibits an alkaline reaction, and afterwards tartaric

acid, until it shows a feeble acid reaction; it is then distilled over the water-bath. Ferrocyanide of potassium, when treated in this manner, yields a distillate free from hydrocyanic acid, because the Prussian blue does not suffer decomposition; but if hydrocyanic acid or cyanide of potassium were present, the distillate contains hydrocyanic acid.

[If the presence of ferrocyanide of potassium in the substance under examination is suspected, the mass may be introduced in the retort without addition of an acid, heated to ebullition, then filtered, the filtrate concentrated by evaporation, and mixed with strong heated alcohol; the ferrocyanide of potassium is precipitated in yellowish-white lustrous scales. If cyanide of potassium was present, it remains dissolved in the alcohol; and if the mass contained free hydrocyanic acid, it will be found in the distillate.]

[§ 84. If, after the methods just described, no hydrocyanic acid has been detected in the vomited matters, the stomach and the intestines, other organs and secretions may be subjected to the same treatment, so ex. gr. the blood, brains, liver, and urine, though it will probably be fruitless. In the brain, the spinal marrow, and the heart, hydrocyanic acid has never yet been detected by reagents, though its presence was clearly indicated by the odor; here, therefore, the odor was evidently a more delicate test than any chemical reagent. In the liver and urine, Orfila could never detect this poison.]

[§ 85. To prove satisfactorily the presence of hydrocyanic acid in a dead body is always, unless the circumstances be very favorable, a pretty difficult mat-

ter. The chances of obtaining a decisive result decrease in proportion to the time which elapses between the administration of the poison and the dissection of the body. It would appear from repeated experiments that, under ordinary circumstances, the chemical examination is not likely to be attended with success when made three days after death, or eight days after death in bodies that have been buried; this, however, should not detain the analyst to undertake an examination at even a later period, since there are a few cases on record where the poison has been found seven, and even twelve, days after death.

A chemical examination of the body is useless, and cannot possibly yield any result if death was produced by inhalation of hydrocyanic acid vapor, or if chlorine or a hypochlorite (ex. gr. bleaching liquid) has been administered as antidote.—*Schneider*.]

[§ 86. From the preceding remarks it is evident that the analyst can never be expected to determine, with the slightest degree of accuracy, the quantity of hydrocyanic in a body; to show its presence is all he can do. Even if the analytical methods for its determination were sufficiently accurate to separate and determine the whole amount of the poison contained in the various organs, the blood, the secretions, etc., a considerable quantity would escape detection on account of its volatility. But there are other cases in which a quantitative determination may be desired. Thus ex. gr. the analyst may be required to examine rests of food and drink for hydrocyanic acid, and to determine whether the

quantity of the poison which they contain is sufficient to have caused death. This question can only be answered by a quantitative analysis, which is conveniently executed in the following manner:

The substance under examination, if a liquid, is accurately weighed, then precipitated with nitrate of silver, afterwards a few drops of nitric acid added, just sufficient to produce a weak acid reaction, and the precipitate collected on a filter; the precipitate is washed with distilled water, dried at 212° and weighed; 100 parts of cyanide of silver correspond to 20.15 parts of hydrocyanic acid. If the liquid contains chlorides, besides cyanides, the precipitate is a mixture of cyanide and chloride of silver. In such a case the liquid has to be divided in two equal parts. With one of them we proceed as just mentioned, and thus obtain the sum of chloride and cyanide. The other is mixed with some borax, evaporated to dryness, and the dry residue exposed to a moderate heat (the heat ought never be driven so high as to cause fusion); the hydrocyanic acid vaporizes, while hydrochloric acid unites with the soda of the borax. The residue is dissolved in water, the solution acidulated with nitric acid, and afterwards precipitated with nitrate of silver; the precipitate is dried and weighed. By deducting the weight of the chloride of silver from the weight of the chloride and cyanide, as obtained by the first experiment, we obtain the weight of the latter.

Solid substances are treated as directed (§ 74), care being taken to connect the retort with a good refrige-

ratory, so that the whole of the vapors may be condensed; the distillate is then treated as in the preceding case.]

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§ 87. [Several plants, which chiefly belong to the division of Drupaceæ, and of which the most important are the bitter almond, cherry laurel, bird cherry, and peach, yield by distillation with water liquids which contain hydrocyanic acid and a peculiar essential oil, the essential oil of bitter almonds. It appears that neither the hydrocyanic acid, nor the essential oil, exist ready formed in the plant, but that they owe their origin to the action of a peculiar albuminaceous substance, emulsine, on a peculiar crystalline principle, named amygdaline, both of which are found in the various parts of the plant. When almond pulps, or the leaves of the cherry laurel, etc., are bruised with water, these two principles come in contact, and the amygdaline is decomposed into hydrocyanic acid, essential oil, and sugar. A gentle heat favors, but a boiling heat prevents, the reaction; alcohol and ether, which, like boiling heat, coagulate the emulsine, also prevent the decomposition. The pure oil of bitter almonds does not possess any poisonous properties, but the crude commercial article exercises poisonous effects in proportion to the amount of free hydrocyanic acid which it contains. The various distilled waters, as bitter almond water, cherry laurel water, peach water, etc., contain very variable quantities of prussic acid, rarely more than 1.5, frequently only 0.1 per cent.

The presence of hydrocyanic acid in these waters

is easily shown, and, if required, the amount quantitatively determined after the method given § 88. To detect its presence in the essential oil of bitter almonds, the oil is gently heated and well agitated with a watery solution of caustic potassa; cyanide of potassium is formed, which may be subjected to the usual tests. Or the oil is mixed, and well agitated with water and some finely pulverized red oxide of mercury. After some time the mixture is distilled, when the oil passes over, and cyanide of mercury remains in the retort.]

CHAPTER IV.

ON THE DETECTION OF OXALIC ACID.

[§ 88. Oxalic acid, when introduced in[illegible] tem, is very rapidly absorbed; it has bee[illegible] the blood of the heart of men who died wit[illegible] hour after the administration of the poiso[illegible] also been detected in the urine. It is, [illegible] quite possible that in a case of poisoning [illegible] acid, nothing of the poison is to be found in [illegible] *mæ viæ*, part of it having been removed by vom[illegible] etc., and the rest having entered into the blood.

To detect the presence of oxalic acid in the contents, or the vomited matters (which should be treated separately), we proceed, according to Orfila, in the following manner:

§ 89. The substances under examination are placed into a large porcelain dish, and boiled with distilled water; the liquid, while hot, is filtered through paper, or cloth. The operation is repeated once more, the two filtrates are united, and evaporated to dryness at a gentle heat. The residue is repeatedly treated with small portions of cold concentrated alcohol, the alcoholic solutions are united and evapo-

rated, at a gentle heat, to a small volume. On cooling, oxalic acid separates in crystals, if it was present in sufficient quantity. The presence of a large amount of organic matter may prevent crystallization. In this case, the organic substances may first be precipitated by the addition of some tincture of nut-galls (previously tested for oxalic acid); the precipitate is separated by filtration, the filtrate evaporated to dryness, and the residue treated with concentrated alcohol—(*Schneider*); on evaporating the alcoholic solution, crystals are deposited. The crystals are dis- water, and the solution tested with the gents.

e solution shows a strong acid reaction. ne-salts produce a white precipitate of lime; if the quantity of oxalic acid is very ew drops of ammonia are added; the pre- n this case, appears sometimes only after a he precipitate is soluble in free hydrochloric ic acid, when added in sufficient quantity; it it very slightly soluble in oxalic, acetic, and other ganic acids; it is insoluble in chloride of ammonium, and other ammoniacal salts. The precipitate is even produced with a solution of sulphate of lime, and by this reaction, which is the most characteristic, oxalic acid is distinguished from all other acids, racemic acid only excepted. Nitrate of silver produces a copious white precipitate of oxalate of silver, insoluble in an excess of oxalic acid, with difficulty soluble in nitric acid, more readily dissolved by ammonia. The precipitate may be collected on a filter, dried, and heated in a porcelain capsule; it is decomposed with a slight detonation and emission of

thick, white fumes, metallic silver remaining behind. When mixed with a solution of chloride of gold, metallic gold is deposited, sometimes in the shape of a yellow crystalline powder, coating the sides of the tube; heat facilitates the reduction; if the solutions were concentrated, carbonic acid escapes with effervescence. If there is sufficient material, a portion of the crystallized acid is introduced into a small flask, provided with a delivery-tube; some pure, concentrated sulphuric acid is poured on the crystals, and a gentle heat applied. The oxalic acid is completely decomposed into carbonic acid and carbonic oxide, which are collected, over water, in a small bell-jar; the remaining liquid is colorless, if the oxalic acid is pure. The mixture of the gases is shaken with lime-water, which, by absorbing the carbonic acid becomes milky from carbonate of lime; the remaining gas, when kindled, burns with a blue flame.

§ 91. If not free oxalic acid, but an alkaline oxalate was used for poisoning, this will not enter into the alcoholic solution, but remain in the residue, obtained by evaporating the watery extract to dryness (v. § 89). This residue may, besides, contain some free oxalic acid, which was left undissolved by the alcohol. It is, for this reason, always advisable, whether free oxalic acid has been detected by the method just described, or not, to subject this residue to the following treatment:

The residue is treated repeatedly with small portions of cold water; the liquids are united, filtered, and the filtrate precipitated with chloride of calcium. The oxalate of lime is collected on a filter, washed with water, and boiled for about half an hour with a

solution of carbonate of potassa. Insoluble carbonate of lime and soluble oxalate of potassa are formed. The former is removed by filtration, the filtrate precipitated with acetate of lead (oxalate of lead is thrown down), the precipitate collected on a filter, and washed with water. To separate the oxalic acid from the lead, the precipitate is suspended in water, and a current of sulphureted hydrogen gas passed through the mixture, until the liquid smells distinctly of the gas. It is then placed at a moderately warm spot, until the excess of the gas has passed off, filtered, and the filtrate, which contains free oxalic acid, evaporated to crystallization. The crystals are tested as above described.

§ 92. The investigation becomes much more complicated when an alkaline earth, as magnesia, or a lime-salt has been administered as an antidote. In this case, a large portion, or the whole, of the oxalic acid remains in the insoluble residue left after boiling the substances with water. By washing with water, the finer particles are separated from the organs, and the mass thus obtained repeatedly treated with water, to effect as complete as possible a separation of the heavy powder from the lighter organic substances, which remain suspended in the liquid and are poured off with it. The impure oxalate is collected and treated with hydrochloric acid, if magnesia was the antidote used. The solution is filtered, and the filtrate neutralized with ammonia; oxalate of magnesia being soluble in ammoniacal salts, no precipitate will be produced. The magnesia is now removed by precipitation with carbonate of potassa; the liquid, separated from the precipitate

by filtration, contains oxalate of potassa; from this the oxalic acid is obtained in the free state by the method above given.

§ 93. If lime, or a lime-salt, was the antidote, the separation of the acid from the base becomes still more difficult. In this case, the impure oxalate (v. § 92), is dissolved in moderately concentrated nitric acid; the solution is gently heated to effect a partial destruction of the organic matters, and, after cooling, precipitated with ammonia. The precipitate, consisting essentially of oxalate of lime, is digested with acetic acid, which dissolves any phosphates which might be present. The oxalate of lime, thus purified, is treated with carbonate of potassa, etc., as described in § 91.

It is not admissible to treat the impure oxalate with carbonate of potassa, because the organic matters which it contains, on being boiled with the alkali, may give rise to the formation of oxalic acid. This objection cannot be raised against the treatment with nitric acid; for, even if oxalic acid should be formed, it will remain in the liquid as oxalate of ammonia; only the pre-existing oxalate of lime being precipitated on the addition of ammonia.]

CHAPTER V.

ON THE DETECTION OF PHOSPHORUS.

§ 94. Chemico-legal investigations for the detection of phosphorus are not of very rare occurrence, especially since friction-matches, and pastes containing phosphorus for killing rats, mice, etc., have come into general use. It is difficult to conceive how willful murder can be perpetrated by poisoning with phosphorus, on account of the very extraordinary and disagreeable odor which it imparts to all kinds of food and drink. [There are, however, cases of this kind on record; one mentioned by Orfila, where two persons, cautioned by the peculiar odor, escaped death, but the third, swallowing the poisoned soup, died of the effects; another case, that of Jean Riehl, is mentioned by Flandin.] Two cases of intended poisoning have come under my observation; in one case it was a paste used for killing rats, and in the other the mass used for friction-matches which were employed; but the odor, in both cases, served as a warning.

§ 95. The odor of phosphorus, undergoing slow oxidation, is so characteristic that its presence in

food, contents, etc., may by this means alone be with certainty ascertained. Food, and other matters, containing phosphorus, become luminous in the dark when agitated and gently heated. Lipowitz remarks that the luminosity is destroyed by ammonia, and that, consequently, in substances which have become ammonial by putrefaction, the phenomenon does not take place. By an addition of dilute sulphuric acid, until the mass shows an acid reaction, the luminosity is restored.

To collect the finely divided particles of phosphorus which are often intimately mixed with, and disseminated through organic and other substances, Lipowitz proposes the use of sulphur. If matters containing phosphorus are heated with some small pieces of sulphur, the latter takes up the phosphorus and forms a compound in which the presence of the poison is readily demonstrated. If the experiment is performed in a retort, the distillate frequently possesses the odor of phosphorus, and its presence here may also be easily detected.

§ 96. The mode of procedure, according to Lipowitz, is as follows: The substances are acidulated with dilute sulphuric acid and introduced into a tubulated retort. A few pieces of sulphur are then added, and, the receiver being loosely fitted on, the distillation is commenced. The contents of the retort having been kept boiling for about half an hour, the operation is discontinued. The distillate is mixed with a little fuming nitric acid, introduced into a porcelain dish, and evaporated; thus the phosphorous acid, originating from the oxidation of the vapors of phosphorus, is converted into phosphoric acid. The

residue is diluted with water, filtered if necessary, and mixed with ammonia in excess. The resulting liquid is tested with a solution of chloride of ammonium-magnesium, or with a solution of sulphate of magnesia previously mixed with a solution of chloride of ammonium. If phosphoric acid is present a white, granular and crystalline precipitate of phosphate of magnesia-ammonia is thrown down.

The contents of the retort are, after cooling, emptied into a porcelain dish, and the small pieces of sulphur taken out and washed with water. If these are placed into a porcelain dish, heated over a water-bath, they become luminous when phosphorus is present; when treated with fuming nitric acid a liquid is obtained in which the presence of phosphoric acid is detected, as above described. A few of the pieces of sulphur may be enclosed in a glass tube filled with water, and handed, as *corpus delicti*, to the authorities. It ought to be remarked here that, with long keeping, the luminosity of the sulphur-pieces is lost, but then phosphoric acid may always be detected in the water.

Lipowitz states that he has detected by this method $\frac{1}{140000}$ of phosphorus in poisoned food with certainty, and even in cases where not a trace of phosphorous acid could be found in the distillate, the presence of phosphorus in the sulphur was satisfactorily shown. (Lipowitz in Pogg. Annalen, vol. xc., p. 600; Pharm. Centralblatt, 1854, p. 157; Schacht in Archiv für Pharmacie, vol. lxvi., p. 165.) Experiments, conducted after this method in my laboratory, have yielded very satisfactory results.

§ 97. Another method for the detection of phosphorus in cases of poisoning has been given by Mitscherlich (Journal für Pract. Chemie, vol. lxiii., p. 238.)

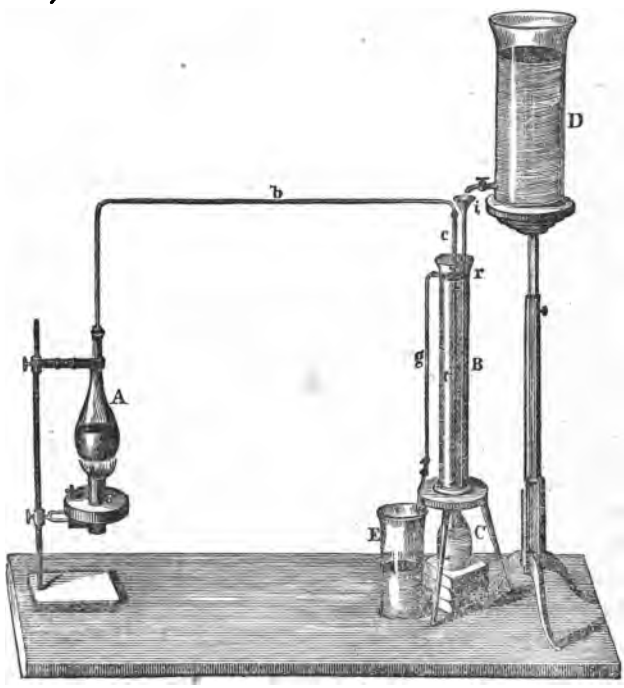

Fig. 11.

The suspected substance is introduced, together with some sulphuric acid, and the necessary quantity of water, into a small flask (A. Fig. 11.) Into the neck of the flask a long horizontal delivery-tube (b) is fastened by means of a perforated cork; the other end of the tube (b) is bent at a right angle, and enters through a cork into the vertical condensing-tube (c)

of a Mitscherlich's condenser. The condenser consists of a tall glass-cylinder (B) perforated at the bottom; through this opening passes the lower, conical end of the condensing-tube; it is fitted in by means of a perforated cork. The cylinder rests on a wooden tripod perforated in the centre. From a vessel (D) a current of cold water is made to flow through the funnel tube (i) to the bottom of the cylinder (B); the hot water rises to the top and escapes through the tube (g) which, by means of a cork, is inserted into an opening at the upper part of the cylinder. A flask (C) serves to collect the distillate.

The flask (A) is then heated until distillation commences. If phosphorus is contained in the contents of the flask, a distinct luminosity, usually a luminous ring, is observed in the dark at the spot where the vapors enter into the upper part of the tube (c). When a mass, weighing five ounces, and containing only $\frac{1}{40}$ of a grain of phosphorus, *i. e.* $\frac{1}{100000}$th part, is thus treated, the luminosity will continue until about three ounces have distilled over, which will take about half an hour. In an experiment, executed in this manner, the distillation was discontinued at this period, and the flask, uncovered, left to rest for fourteen days; when the distillation, after this time, was resumed, the luminosity appeared as before.

If there are in the liquid substances which destroy the luminosity of phosphorus, as ether, alcohol, and oil of turpentine, no emission of light is perceptible as long as these distill over. In the case of ether and alcohol, which are very volatile and pass over very soon, the luminosity appears after a short while; but

if oil of turpentine is present, the phenomenon cannot be observed.

At the bottom of the flask which receives the distillate, the phosphorus collects in small globules. In an experiment, where five ounces of substance, containing one-third of a grain of phosphorus, were treated after this method, so many globules of phosphorus were obtained, that one-tenth part of them sufficed to prove them to be phosphorus. One portion of the globules may be thrown on a filter, and washed with alcohol; on being then placed on a warm spot, the phosphorus melts and ignites spontaneously. Another portion of the globules, and the liquid which, on distillation, exhibits luminosity, may be handed to the authorities.

If large quantities, containing a considerable amount of phosphorus, are subjected to distillation, sufficient phosphorous acid is produced (by oxidation of the phosphorus vapors), that its presence in the distillate may be detected by nitrate of silver and protochloride of mercury; or it may be converted into phosphoric acid by oxidation with nitric acid.

Mitscherlich observes that no importance ought to be attached to the reactions which the distillate may give with nitrate of silver and protochloride of mercury, since volatile animal matters, which also act reducing on these salts, may condense in the receiver. He also observes that, on distilling from a retort, the contents of which are kept boiling, it cannot very well be avoided that some particles of the liquid are carried over mechanically into the receiver, and thus the distillate may become mixed with phosphoric acid.

CHAPTER VI.

ON THE DETECTION OF ALCOHOL AND CHLOROFORM.

§ 98. The detection of alcohol in the body, in cases of death from alcoholic liquors, will, as a general thing, be more of scientific than of practical interest. The investigation will always be successful if commenced soon after death, or if the substances for examination, contents, lungs, etc., were preserved in well-closed vessels. It is good to have the vessels tied over with bladder.

The first thing to be observed is the odor and the reaction of the substances under examination. The contents of the stomach of persons who died of the effects of alcohol, show usually a decided acid reaction, owing to the presence of acetic acid. In this case, the acid is neutralized with carbonate of soda, avoiding an excess of the alkali.

The mass is then placed in a retort which is heated over a water-bath. The retort is connected with a receiver, or better, with a refrigeratory. The distillate is rectified by a second distillation with addition of a sufficient quantity of dry carbonate of potassa, or chloride of calcium. For this second distillation, a small tubulated retort may be used, or a small

flask, into the neck of which a long, bent glass-tube, of several feet in length, and from one-quarter to one-third of an inch in diameter, is fitted by means of a perforated cork. The tube must be of thin glass and bent at its lower extremity, in such a manner as to reach into a small glass-bottle, for the reception of the distillate. The tube is surrounded by blotting-paper, which is constantly kept wet with water, and thus serves as a condenser. Into the flask, or retort, first the liquid, then the carbonate of potassa, or chloride of calcium, is introduced. A large porcelain dish may serve as a water-bath. No rules can be given as regards the quantity to be distilled over; this must be left to the judgment of the analyst.

§ 99. If the distillate does not contain too small a quantity of alcohol, it is already detected by its odor. But whether the odor is noticed, or not, the distillate should be subjected to the following tests:

When poured on a hot plate, or when heated in a platinum-spoon, it burns, even if but little alcohol is present.

When heated with chromic acid, or with chromate of potassa and sulphuric acid, the chromic acid is reduced, sesquioxide of chromium is formed, and the liquid assumes a green color. If the operation is performed in a small retort, which is connected with a well-refrigerated receiver, a liquid containing aldehyde is obtained; on heating this liquid with caustic soda, it assumes a yellow, or brownish color, and emits a peculiar, cinnamon-like odor.

A small portion of the distillate is poured on a porcelain plate, on which a watch-crystal is placed, which contains some platinum-black, free from acid.

The whole is covered with a bell-jar, or a beaker-glass. The alcohol is converted into aldehyde and acetic acid; the latter is easily recognized by its odor and its acid reaction.

[If the analyst has a comparatively large quantity of alcohol at his disposal, the conversion into acetic acid may be effected in the following manner: A glass-rod is loosely fitted into the neck of a small glass funnel; into the latter some platinum-black is placed, and moistened with a few drops of distilled water. The alcoholic liquid is then made to flow very slowly on the platinum-black, which is effected by means of a cotton string, serving as a syphon. The acid liquid which drops down from the funnel, is carefully neutralized with a very dilute solution of caustic potassa, and evaporated to dryness over a water-bath. The acetate thus obtained, may then be tested with the usual reagents for acetic acid.

The platinum-black for these experiments is most conveniently prepared, by placing a zinc-rod in a dilute solution of bichloride of platinum, and washing the precipitate with hydrocholoric acid, then with nitric acid, and finally with a solution of caustic potassa.]

If a sufficient quantity of the distillate is obtained, its specific gravity may be ascertained, by weighing it in a small bottle, and thus the amount of alcohol can be determined.

§ 100. Buchheim recommends the following method for the detection of very minute quantities of alcohol. The substances under examination, previously neutralized with caustic or carbonate of soda, if necessary, are placed into a tubulated retort, the

neck of which has been cut off far enough, to allow the introduction of a capsule of platinum, silver, glass, or porcelain. The capsule into which some platinum-black is laid, is placed into the neck of the retort at the spot where it joins the body. At each end of the capsule, a piece of moistened litmus-paper is fastened, so as to be partially in contact with the platinum-black. The distillation is performed over a water-bath. As soon as the first drops of liquid appear in the neck of the retort, that part of the litmus-paper which is in contact with the platinum-black becomes reddened, even if but traces of alcohol are present. The rest of the paper remains blue, proving to evidence, that the acid does not come from the contents of the retort, but originates within the platinum-black. [If the operation has proceeded for some time, so that some drops of liquid have already flown out from the beak of the retort, and the litmus-paper remained unchanged, it may safely be concluded, that there is no alcohol present. But if the paper begin quickly to redden, the capsule may be withdrawn, and the beak connected with a receiver. The distillate is rectified as above described.]

§ 101. Morin (*De l'alcool considéré sous le rapport toxicologique, par M. Morin*), has communicated to me a case, where a strong odor of ether was noticed at the dissection of a man, who had drowned himself in a state of drunkenness. The contents of the stomach, previously neutralized with carbonate of soda, were distilled; a slightly opalescent liquid of distinct ethereal odor was obtained. The distillate was mixed

with pure carbonate of potassa, as long as fresh portions of the salt dissolved in the liquid, and left to rest. After some time, a thin layer of liquid separated, which possessed the odor of ether, and was combustible.

Morin is inclined to think that under certain circumstances, alcohol in the stomach may be converted into ether.

§ 102. The separation of chloroform from the matters with which it is mixed, and its detection in the body, is effected in the same manner as that of alcohol.

If a liquid containing chloroform is introduced into a flask, into the neck of which a glass-tube, bent at a right angle, is inserted by means of a perforated cork, if the liquid is then heated, while a portion of the horizontal part of the tube is kept red-hot, the vaporized chloroform is decomposed into carbon, hydrochloric acid, and chlorine. If a slip of paper, impregnated with starch-paste containing iodide of potassium, is held into the open tube, it becomes blue. (*Ragsky*, Orfila's Toxicology). This method, by which the smallest quantities of chloroform may be detected, has proved, by experiments executed in my laboratory, to be very correct and delicate.

In regard to the execution of the experiment, the remark might not be superfluous, that the tube ought to be heated to redness, and the paper introduced before heat is applied to the liquid, because the blue compound of iodine with starch is destroyed by heat. If, therefore, the liquid is heated to ebullition

before the paper is introduced, the heat of the vapor will prevent the formation of the characteristic compound. The color may, of course, disappear after a while, by either heat, or an excess of chlorine.

CHAPTER VII.

ON THE DETECTION OF POISONOUS ALKALOIDS.

[illegible]03. Cases of poisoning with alkaloids are of comparatively rare occurrence [in countries where the laws of a well-regulated medical police restrict the sale of these dangerous drugs. In England, and in this country, where such restrictions are wanting, very many cases of fatal poisoning with these substances are known, at least a sufficient number to make the knowledge of exact and reliable methods for their detection, appear very desirable.]

For some alkaloids, when in the pure state, we have very characteristic tests, not less so than for the inorganic poisons; thus, for instance, for strychnine and morphine; but the separation, in the pure state, of very minute quantities of these poisons from the contents, food, etc., requires a very high degree of practical knowledge, and a most practiced hand; and yet, their separation in the purest condition possible, is necessary; because a very minute intermixture of any foreign substance, frequently renders the tests used for their detection fallacious.

For other alkaloids, again, we are utterly destitute

of characteristic tests; and in such cases we must consider ourselves very fortunate, if we can show that there is any alkaloid present. To ascertain the poisonous effect of the separated alkaloid, the quantity obtained is usually too small, and with regard to the chemical tests, it must be borne in mind, that the alkaloids show, in this respect, a great similarity.

It is a very fortunate circumstance, that in the majority of cases there is but very little doubt in regard to the nature of the poison employed, and all that remains to be done by the legal chemist, is to show that the poison really existed in the body, etc. For this reason, the chemical examination has, not unfrequently, more a scientific than a practical interest.

§ 104. The separation of the alkaloid, in the purest possible condition, is, as mentioned above, to be aimed at before all other things; to ascertain its nature, constitutes the next step. Of the alkaloids which may become the objects of our investigation, some are volatile, as nicotine, conicine, etc., others non-volatile, as morphine, strychnine, veratrine, etc. We shall commence with describing their most characteristic properties and tests.

Nicotine.—It is a colorless, oily liquid, becoming yellow on exposure to air, of acrid taste, and of a faint odor; it is usually said to possess the odor of tobacco, but I should rather call it an ethereal odor, which is most distinctly noticed in the dilute state. It is readily soluble in ether and alcohol; water and alcohol dissolve it in considerable quantity. The alcoholic solution affects tumeric-paper. On distillation with

water, it passes over with the watery vapors; when distilled alone, it is partially decomposed.

With acids, it forms non-volatile salts, which are soluble in water and in alcohol, but not in ether. On mixing the solution of a salt of nicotine with caustic soda and ether, the liberated alkaloid dissolves in the latter, and on evaporating the ethereal solution it remains behind as an oily drop. On distilling a salt of nicotine with a solution of caustic soda, there results a distillate containing nicotine. In order to obtain the whole of the alkaloid, it is advisable to add some water to the contents of the retort, as soon as they become too concentrated, and to repeat the distillation.

If a distillate containing nicotine is neutralized with oxalic acid, and afterwards evaporated, oxalate of nicotine remains behind; if the distillate contained ammonia, as will usually be the case, it is mixed with some oxalate of ammonia. Alcohol dissolves the oxalate of nicotine, but does not affect the oxalate of ammonia; by this means the two may be separated. The alcoholic solution yields, on evaporation, the oxalate of nicotine.

If another acid, ex. gr. tartaric, sulphuric, hydrochloric acid, is chosen to effect the neutralization of a distillate containing nicotine, it is evident that the corresponding nicotine-salt is obtained. In using sulphuric acid, an excess must be avoided, lest the mass might become charred. The removal of fatty substances may be effected by dissolving the salt in water, or by washing with ether.

To reagents, nicotine and its salts behave as follows:

Terchloride of gold produces in a watery solution a reddish yellow precipitate, readily soluble in an excess of nicotine.

Bichloride of platinum causes a yellow precipitate; the solution must be perfectly free from ammonia; this may be effected by continued heating, or by the treatment of a nicotine-salt with alcohol.

A solution of nicotine causes precipitates in solutions of neutral and basic acetate of lead, in acetate of copper, in chloride of cobalt, and in many other metallic salts. [Chlorine-gas decomposes nicotine with evolution of hydrochloric acid gas, and formation of a blood-red liquid, which on exposure to the rays of the sun, becomes colorless.]

On adding a solution of iodine (prepared from iodine, water, and a little iodide of potassium), to a solution of nicotine, a yellow precipitate is thrown down; this precipitate disappears after some time, but on adding more of the iodine-solution, a copious precipitate of a kermes-brown color is produced (ammonia decolorizes a solution of iodine).

A solution of tannine produces a copious white precipitate.

A solution of chloride of nicotine gives, with bichloride of platinum, a yellowish-red, crystalline precipitate, which is a double chloride of platinum and nicotine, and which is with difficulty soluble in water, and insoluble in alcohol and ether. From a dilute solution, the compound separates in pretty large prisms. If the nicotine contained ammonia, the double chloride of platinum and ammonium is formed at the same time; this compound is immediately produced; in order to obtain the nicotine dou-

ble-salt separate, the liquid is rapidly filtered off from the precipitate; the double chloride of platinum and nicotine is gradually deposited from the filtrate.

[If nicotine is added in small portions to a luke-warm, acid solution of protochloride of platinum, care being taken that the temperature do not rise too high, orange-yellow crystals of a double chloride of platinum and nicotine are obtained. On pouring off the mother liquor and evaporating, red prismatic crystals of another double chloride are formed.]

Terchloride of gold produces in solutions of the salts of nicotine a yellow, flocculent precipitate, which dissolves with difficulty in hydrochloric acid. A solution of iodine produces a kermes-brown, and a solution of tannine, a whitish precipitate.*

Of all the reactions for nicotine, its volatility is the most characteristic; only conicine shows a similar behavior, but this is easily distinguished by its odor, and by being much less soluble in water.

§ 105. *Conicine.*—This alkaloid is, like nicotine, an oily, colorless liquid, which becomes yellow on exposure to air. Its odor, which is represented as resembling that of young mice, is exceedingly disagreeable and benumbing, and much more distinct, than that of nicotine; its taste is acrid. It is readily soluble in alcohol and ether. [With the vapors of nitric, hydrocholoric, and acetic acid, it forms thick white fumes. It coagulates albumen.] Water does not take up so much of this alkaloid as of nicotine; hence it is, that by being shaken up with not too large

* Compare: Chemie der organischen Alkalien, von Hartung-Schwarzkopf. München, 1855.

a quantity of water, it is divided into drops, and on resting, collects again on the surface as an oily layer. On adding some caustic soda to a moderately concentrated solution of a salt of conicine, the liquid becomes milky, owing to the separation of the alkaloid in minute drops, like an essential oil; on resting for some time, these drops unite and form an oily layer on the surface. On spontaneous evaporation of its ethereal solution, it remains behind, as a yellowish, oily drop. Its alcoholic solution colors turmeric-paper brown, with a purple tinge.

Mixed with water and an acid, salts are formed, and the peculiar odor of the alkaloid disappears. On evaporating the solution of a salt of conicine, it assumes a brownish color, and the residue contains some ammonia; this even takes place if the temperature is kept very low. An excess of a strong acid, most especially of sulphuric acid, acts destructively. The salts are readily soluble in water and alcohol; insoluble, or nearly so, in ether.

On addition of caustic soda to the solution of any of its salts, the alkaloid is liberated, and its peculiar odor becomes perceptible; on distilling, the conicine passes over with the watery vapors. By neutralizing the distillate with oxalic acid (an excess of which is not injurious), and evaporating, oxalate of conicine is obtained; a subsequent treatment with alcohol may be resorted to, for the purpose of purifying it from an admixture of oxalate of ammonia; the latter is insoluble in alcohol, while the former is taken up by this solvent.

Conicine and its salts behave to reagents in essentially the same manner as nicotine and its salts.

In a solution of terchloride of gold, conicine produces a light-yellow precipitate.

In a solution of bichloride of platinum, it produces a similar precipitate; absence of ammoniacal salts is necessary.

In a great many other metallic salts it causes precipitates, resembling those produced by ammonia.

On adding a solution of iodine (prepared from iodine, water, and a particle of iodide of potassium) to a watery solution of conicine, a kermes-brown precipitate is thrown down. With very little solution of iodine only, a turbidness of sulphur-yellow color is produced, and the liquid becomes, after a short time, colorless.

A solution of tannine causes a whitish turbidness and precipitate.

On gradually adding chlorine-water to a watery solution of conicine, the liquid becomes white and turbid.

[On passing a current of chlorine-gas through conicine, thick white fumes are formed at first; after a while, the temperature commences to rise, and the liquid assumes a blood-red color; on continuing the operation, the liquid becomes again colorless, thickens, and is finally converted into a white, crystalline mass.]

In solutions of the salts of conicine terchloride of gold produces a light yellow, and a solution of iodine a kermes-brown precipitate.

From nicotine the conicine is best distinguished by its odor and by its inferior solubility in water; also by the color of the chloride of gold precipitate which is of a lighter yellow in the case of conicine,

and by the reaction with chlorine-water, which does not produce a whitish turbidness with nicotine.

§ 106. *Morphine.*—It occurs in small, colorless prisms, or as a crystalline powder. It is little soluble in water, more so in alcohol, especially on boiling. Ether dissolves only a very small quantity. A solution of caustic soda dissolves a considerable portion. With acids it forms salts, which are soluble in alcohol. The sulphate, acetate, and chloride of morphine are soluble in water, the latter not to a great extent. The chloride crystallizes easily in long delicate prisms. An excess of acid increases their solubility; even those salts which are insoluble in pure water dissolve in presence of an excess of acid. The most important reactions of morphine are as follows:

On adding morphine to concentrated nitric acid, the latter assumes a blood-red color, which gradually passes into yellow.

On adding morphine, or a salt of morphine, to a solution of iodic acid, iodine is set free; the iodine either falls to the bottom or remains dissolved in the liquid, imparting to it a brown color. The liberated iodine is recognizable by the odor. If some starch was previously added to the solution of iodic acid, this becomes, of course, blue, on addition of the morphine.

[It must be borne in mind that albuminous liquids, lithic acid, and many other organic compounds, act in this manner on a solution of iodic acid. The test is, therefore, not conclusive.]

A neutral solution of sesquichloride of iron produces in a neutral, or nearly neutral, solution of a

salt of morphine, a blue precipitate. The blue color soon passes into a dirty green and brown.

[The color is destroyed by alcohol, and by acetic ether; also by heat. In presence of meconic acid the color is red, instead of blue.]

Bichloride of platinum gives a granular orange-yellow precipitate.

From a solution of terchloride of gold the metal is gradually reduced.

Some morphine is placed in a small porcelain dish, a few drops of concentrated sulphuric acid are added, and heat is applied until solution has taken place. On diluting with a little water, and placing a particle of chromate of potassa into the liquid, the latter assumes an intensive mahogany-brown color.

§ 107. *Narcotine.*—It crystallizes in pretty large, colorless, lustrous prisms, less frequently in scales. It is insoluble in water. It requires 100 parts of cold, and 20 parts of boiling alcohol for its solution. Ether dissolves on boiling $\frac{1}{50}$th of its own weight of narcotine; from an ethereal solution it is deposited, on evaporation, in comparatively large prismatic crystals. With acids it forms salts, all of which possess an acid reaction, and an exceedingly bitter taste.

It is distinguished from morphine, 1st, by its solubility in ether; 2d, by its insolubility in water containing acetic acid (by either of these two solvents it may be separated from morphine); 3d, by not producing a blue color with sesquisalts of iron, and, 4th. by its reaction with sulphuric acid, containing a trace of nitric acid. This test, which is the most

characteristic for narcotine, is executed in the following manner:

Some nicotine is placed in concentrated sulphuric acid, to which a very slight quantity of nitric acid has previously been added, and heat applied; the liquid assumes a blood-red color [which disappears again on addition of more nitric acid.]

§ 108. *Strychnine.*—Strychnine occurs either in white, lustrous prisms, or octahedrons, or as a white powder. It is very little soluble in water and ether, more soluble in alcohol, especially on boiling. With acids it forms salts which are soluble in alcohol; the sulphate, nitrate, and chloride are also dissolved by water. In presence of free acid, even those which are only slightly soluble in pure water, become soluble. Nitrate of strychnine crystallizes readily in long, slender prisms.

Its most important reactions are as follows:

Strychnine and its salts possess an exceedingly bitter taste. [The taste is, according to Christison's recent trials, the best "guide test." He has found no indication by the color-test beyond the 15,000th of a grain of pure strychnine in distilled water, while he perceived the sense of bitterness in distilled water when the strychnine formed only the 40,000th of a grain.—*Taylor*, "On Poisoning by Strychnine," p. 113.]

A solution of tannine, with the solution of a salt of strychnine gives a white precipitate.

Sulphocyanide of potassium gives a white, crystalline precipitate.

Terchloride of gold gives a reddish-yellow precipitate.

Bichloride of platinum gives a yellow, granular precipitate.

Chlorine-water gives a white precipitate, which is soluble in ammonia. [If a current of chlorine-gas is passed through a very dilute solution of strychnine, every gas-bubble, as it rises through the liquid, becomes surrounded with a white coating; on arriving at the surface, it breaks and sinks to the bottom in the shape of a white crystalline powder, which is insoluble in water, even on boiling, but soluble in alcohol and ether. If chlorine-gas is passed through a solution of nitrate of strychnine, a white precipitate is produced; when separated from the liquid by filtration, and treated with sulphuric acid, it assumes a fine rose-color.—*Schlienkamp.*]

On adding strychnine to nitric acid of moderate strength, the liquid assumes a yellow color. Strychnine containing brucine produces, under the same circumstances, a red color, similar to that produced by morphine. [With concentrated nitric acid, the color is in the first moment rose-red, then brown-yellow, and afterwards light yellow.]

On dissolving strychnine in a few drops of concentrated sulphuric acid, and placing in the liquid a small crystal of bichromate of potassa, the acid assumes, round the crystal, a beautiful blue or violet color. Instead of this salt, the deutoxide of lead, or, according to Davy, ferrocyanide of potassium may be employed. In my opinion, the bichromate of potassa deserves, after all, the preference. If the

experiment is executed with the necessary care, the strychnine, deposited from one drop of an ethereal solution, can be very distinctly recognized by means of a drop of sulphuric acid and a particle of the bichromate. But, to obtain a distinct reaction, it is requisite that the amount of bichromate be proportional to the quantity of the alkaloid, and this is best attained by using the former in the shape of a solid piece, [illegible] neither as a powder nor in solution. After solution [illegible] strychnine has been effected, the acid is spread [illegible] over the surface of the porcelain dish, and then the crystal of the bichromate placed in it. On inclining the dish, violet stripes are noticed flowing from the salt, and on moving the crystal back and forward by means of a glass rod, the whole of the liquid assumes a rich violet color. A case has come under my observation where the alkaloid was not, at first, with certainty recognized, because it was present in considerable quantity and was mixed with too little of the bichromate. In using a solid piece of the salt, the color should always appear very distinctly round the crystal; the latter should then be removed to another place, lest the reaction be destroyed by an excess of the salt.

[For the detection of extremely minute quantities of strychnine, the following *modus operandi* has been proposed by Drs. Rogers and Girdwood (Lancet, October, 1856).

A portion of the solution containing the poison, and which should be one in chloroform, should be sucked into a tube, with a fine capillary termination, and evaporated on a piece of white porcelain, in as small a space as possible. This can readily be done by

holding the tube perpendicularly, and touching a piece of white porcelain, previously warmed, with the point, when a small quantity of the solution will escape and evaporate, and repeating this process, until a sufficient quantity for testing be left on the spot. When the porcelain is quite cold, the spot should be moistened, by means of a glass pen, with sulphuric acid, to which a small quantity of a saturated solution of bichromate of potassa has been added, when the characteristic tint of strychnine will appear. The sulphuric acid employed in the above experiment, is prepared by adding, by means of a glass rod, a saturated solution of bichromate of potassa, until it imparts a feeble yellow tint. It is of the utmost importance, for the success of the experiment, that this reagent should be recently prepared, as the chromic acid is soon converted into sesquioxide of chromium, which combines with the sulphuric acid—a change which takes place with extreme rapidity, under the influence of light, of course rendering the mixture useless. The solution of the strychnine should be in chloroform, for the simple reason that, while the other fluids, such as ether, have a remarkable tendency to spread over the surface on which they are put for evaporation, and so dilute, as it were, by extension, chloroform, by having a contrary tendency, leaves the strychnine on a smaller space than the fluid occupied at the moment of its transferrence to the porcelain.

Whether this process does really enable us to detect *the millionth part of a grain without difficulty*, as the authors of it pretend, might, by some, be considered a question open to discussion.

We are indebted to Dr. Marshall Hall for a very delicate physiological test for strychnine. It consists in placing a frog in the watery solution of strychnine or one of its salts; after a time, varying with the strength of the solution, the animal becomes violently tetanic. M. Hall recommends young frogs just taken from the ponds or mud; before placing the animal in the liquid under trial, its back should be cleaned with blotting-paper. In one experiment $\frac{1}{400}$th of a grain of acetate of strychnine was dissolved in six drachms of water, and the frog placed in it; in three hours and a half it became violently tetanic. M. Hall states to have detected by his method the $\frac{1}{56000}$th part of a grain of strychnine; he poisoned a cat with $\frac{1}{6}$th of a grain of acetate of strychnine, and with the contents of the stomach, after some time, three frogs were killed.

Dr. Harley proposes to inject the suspected liquid into the thoracic or abdominal cavity of the frog, stating that the $\frac{1}{1000}$th part of a grain, when thus administered, causes tetanus in three minutes, while it took at least an hour and a half when the frog was placed in the solution. On injecting a solution, containing only $\frac{1}{16,000}$th of a grain of acetate of strychnine, into the lungs of a very small frog, the animal became violently tetanic in nine and a half minutes, and died in two hours.]

[§ 109. *Brucine.*—It forms usually a white crystalline powder, more rarely distinct crystals. It is very little soluble in water, insoluble in ether, easily soluble in alcohol. The aqueous solution possesses an intensely bitter taste. With acids, it forms salts

which, for the most part, crystallize from watery solutions; some of them are also soluble in alcohol.

On passing chlorine-gas through a solution of chloride of brucine, the liquid assumes a yellow, and afterwards a red color. On continuing the operation a white precipitate of the alkaloid is produced, and the liquid becomes clear and colorless. If heat is then applied, the brucine is again dissolved, and the red color reappears with the same intensity; it then remains permanent.—(*Schlienkamp.*)

Nitric acid dissolves brucine; the liquid is at first bright red, then yellowish-red, and becomes yellow on application of heat; if then some protochloride of tin is added, the color changes to violet; the presence of strychnine does not interfere with the reaction. By this change of color, brucine is easily distinguished from morphine.

With concentrated sulphuric acid it becomes in the first moment rose-red, soon after colorless; on adding to the mixture some concentrated nitric acid, it becomes reddish-brown, brownish-yellow, yellow.]

[§ 110. *Aconitine.*—It occurs as a colorless mass, of vitreous lustre, sometimes in granular crystals of acrid taste, of strong alkaline reaction; very little soluble in water, more soluble in ether, and readily dissolved by alcohol. With acids it forms salts which do not crystallize.

In its behavior towards reagents, there is nothing characteristic: it gives precipitates with tannine, solution of iodine, terchloride of gold, corrosive sublimate, and sulphocyanide of potassium. With bichloride

of platinum, it gives no precipitate (distinction from colchicine).

The best tests for this alkaloid, are the physiological. According to Dr. F. W. Headland (Lancet, July, 1856), $\frac{1}{20}$th of a grain will suffice to show them. An alcoholic solution should be given to animals: $\frac{1}{300}$th of a grain will poison a mouse, with characteristic symptoms; $\frac{1}{100}$th a small bird; $\frac{1}{1000}$th of a grain causes tingling and numbness of the tip of the tongue; $\frac{1}{100}$th of a grain dissolved in spirit, and rubbed into the skin, causes loss of feeling, lasting for some time].

[§ 111. *Atropine.*—It occurs crystallized in white silky needles, or as a colorless, vitreous mass. It requires 300 parts of water to its solution; alcohol and ether dissolve it readily. With acids it forms salts, which do, for the most part, not crystallize, and which are easily soluble in water and alcohol. Atropine and its salts are of very little stability; on exposure to air, they suffer gradual decomposition.

Its reactions show nothing very characteristic:

Terchloride of gold produces a sulphur-yellow, crystalline precipitate, which is slightly soluble in hydrochloric acid.

Bichloride of platinum gives a pulverulent precipitate, which balls together into lumps, like resin; it is easily soluble in hydrochloric acid.

Iodide of potassium and sulphocyanide of potassium give no precipitates.

Nitric acid causes no change. Sulphuric acid dissolves the alkaloid, and, on applying heat to the

liquid, it becomes at first red, then black, and sulphurous acid is evolved.

The most characteristic test is its action on the eye. A few drops of a solution of 1 part of sulphate of atropine in 9600 parts of water cause a considerable dilatation of the pupil, lasting from thirty to sixty minutes.

From the investigations of Planta it would appear that atropine and daturine are identical.]

§ 112. *Veratrine.*—Veratrine is a white powder, of burning taste, nearly insoluble in water, soluble to some extent in ether, and easily soluble in alcohol. With acids it forms salts, which are soluble in water.

Placed in concentrated sulphuric acid, the liquid assumes a yellow color, which, on gently heating, passes into yellowish-red, and finally into a beautiful violet-red.

Its dust causes the most violent sneezing.

§ 113. *Colchicine.*—[From an alcoholic solution to which some water has been added, it crystallizes in colorless prisms and needles. On evaporating an alcoholic or ethereal solution of the alkaloid, it is obtained as a transparent, amorphous mass. It is soluble, to some extent, in water (distinction from veratrine); its taste is bitter and acrid; it does not cause sneezing. With bichloride of platinum it gives a yellow precipitate.]

To a solution of iodine, tannine, and other reagents, it behaves like most other alkaloids. Its most char-

acteristic reaction is the dark-violet, or blue color, which it imparts to concentrated nitric acid.

[§ 114. *Hyoscyamine.*—It is sometimes obtained in silky needles, but mostly as an amorphous, translucent mass. When perfectly pure, it is inodorous; the impure alkaloid possesses a very disagreeable odor, resembling that of tobacco; it has an acrid taste. It is soluble in water, alcohol, and ether; the solutions show alkaline reactions. With acids it forms salts, which do not very readily crystallize.

It is a very unstable substance, and does not give characteristic reactions with the usual reagents.

Sulphuric acid colors it brown.

Concentrated nitric acid dissolves it to a colorless liquid.

Hyoscyamine and its salts cause a dilatation of the pupil, a property which it has in common with atropine and some other organic bases, derived from the natural family of the solanaceæ.]

§ 115. *Picrotoxine.*—Picrotoxine is the poisonous principle of the berries of *Menispermum Cocculus.* It forms white crystals, which are soluble in about 150 parts of water, easily soluble in alcohol and ether. Its solubility in water is not to any great extent increased by the addition of an acid, because it does not combine with it; it is more soluble in water containing caustic soda than in pure water, exhibiting rather the character of an acid. For this reason, and because it does not contain any nitrogen, it does not properly belong to the alkaloids.

If a few drops of a solution of blue vitriol are

added to an alkaline solution of picrotoxine, and a gentle heat be applied, a reduction of the protoxide of copper to red suboxide takes place. It behaves, in this respect, like grape-sugar, and many other indifferent organic substances (*Becker*, Archiv. der Pharm. Vol. II. 85. p. 22). Ether, though otherwise a good solvent for picrotoxine, does not take up any appreciable quantity from an alkaline solution.—(*Poellnitz.*)

§ 116. M. Stas has published a very excellent method for the detection of the alkaloids in medico-legal cases (*Recherches médico-légales sur la nicotine, suivies de quelques considérations sur la manière générale de déceler les alcalis organiques dans les cas d'empoissonement*, in the *Bulletin de l'Académie royale de Belgique;* see also *Ann. der Chemie und Pharm.* Bd. 84. p. 379). His method is founded on the observation that the alkaloids form acid salts, which are soluble in water and in alcohol; and that, on decomposing a solution of this kind by means of an alkali, and agitating it with a sufficient quantity of ether, the liberated base dissolves in the ether.

If contents, food, etc., are to be examined, they are mixed with double their weight of alcohol, which should be pure and as strong as possible; from ½ to 2 grammes (from 8 to 30 grains Engl.) of tartaric or oxalic acid are added, and the mass heated, in a retort, or a flask, to about 70° or 75° C. Organs, as liver, lungs, etc., must be cut into small shreds, moistened with alcohol and acid, then pressed, and this operation several times repeated.

When cold, the liquid is strained through filtering-paper, and the residue washed with strong alcohol.

The filtrate is evaporated at a temperature not surpassing 35° C., either in a strong current of air, or, better still, in vacuo over sulphuric acid.

If, after evaporation of the alcohol, fatty, or other insoluble substances separate, the liquid is again passed through a filter, previously moistened with water. The filtrate, together with the washings, is placed under a bell-jar over sulphuric acid, until it has become nearly dry.

§ 117. The residue, from this operation, is exhausted with cold, anhydrous alcohol; the extract is evaporated; the residue is dissolved in the smallest possible quantity of water, and the solution mixed with some pulverized bicarbonate of soda or potassa, until the disengagement of carbonic acid ceases. The liquid is then agitated with from four to six times its volume of pure, rectified ether (free from oil of wine). When the ether has collected on the surface to a perfectly limpid layer, a small portion of it is placed in a watch-crystal, and exposed to spontaneous evaporation.

If a volatile alkaloid (conicine, nicotine) is present, there remain, after evaporation of the ether, oily stripes, which, on application of a gentle heat, collect to a drop and emit the peculiar odor of the alkaloid, more or less disguised by that of the animal matter.

If the substances under trial contained a non-volatile alkaloid (morphine, strychnine, etc.), there remain more or less distinct traces of a solid residue.

§ 118. If the indications, thus obtained, point to the presence of a volatile alkaloid, the contents of the vessel, from which a small portion was taken for

evaporation, are mixed with one or two cubic-centimeters of a concentrated solution of caustic potassa or caustic soda, and the whole well agitated. The ether having again collected on the surface, it is poured off, and the residue thoroughly exhausted by repeating this treatment with fresh portions of ether, three or four times. The ethereal solutions are united.

To this ethereal solution are added one or two cubic-centimeters of water, previously mixed with one-fifth of its weight of pure sulphuric acid; the mixture is well agitated for some time, then left to rest, the ethereal liquid poured off, and the aqueous solution washed with a fresh portion of ether.

The aqueous liquid contains the sulphates of nicotine and conicine, and also of ammonia, if these bases were present. The ether has taken up all animal matters. If conicine is present, a small portion of the sulphate will be found in the ethereal liquid, since this salt is not quite insoluble in ether. Left to spontaneous evaporation, the ethereal solution deposits a small quantity of a yellow residue, of disagreeable odor.

§ 119. The alkaloid must now be separated from the watery solution, in which it is contained in combination with sulphuric acid. For this purpose, the liquid is mixed with a solution of caustic soda, or caustic potassa, until it shows an alkaline reaction, well agitated, and subsequently treated with ether, which takes up the alkaloid and ammonia. The ethereal solution is exposed to spontaneous evaporation; nearly the whole of the ammonia vaporizes, while the alkaloid remains behind. In order to

remove the last trace of ammonia, the dish containing the alkaloid is placed for a moment in vacuo, over sulphuric acid. We thus obtain the alkaloid in the pure state; to ascertain its nature, we must now carefully examine its physical and chemical properties.

Conicine is easily distinguished from nicotine by its penetrating and benumbing odor. When mixed with a little water, it floats on its surface as an oily drop, while nicotine dissolves. If, to this mixture of conicine and water, some chlorine-water is added, drop by drop, a white precipitate is produced (v. § 105). If, to this mixture, or solution, of alkaloid and water, a solution of iodine is added, a sulphur-yellow precipitate is at first produced; on addition of a larger quantity of the reagent, a brown, hydrous precipitate is thrown down. The same liquid gives yellow precipitates with terchloride of gold and with bichloride of platinum. On neutralizing the alkaloid with oxalic acid, its odor disappears, and is again brought forth on addition of caustic soda (v. § 104–105).

§ 120. If the indications, obtained by evaporating a portion of the ethereal solution (§ 117), do not point to the presence of a volatile alkaloid, the contents of the vessel from which this portion was taken are treated in the same manner as described § 118. But to effect a complete solution of the alkaloid, a larger quantity of ether is required, because the fixed poisonous alkaloids are only little soluble in this liquid.*

* It is the insolubility in ether of the salts of the alkaloids which enables us to free them from substances soluble in this liquid, and which would otherwise prevent their crystallization, and interfere

The different ethereal solutions are united, and exposed to spontaneous evaporation. There remains either a solid residue, or a colorless, milky liquid, in which solid particles are held in suspension. It smells strongly of animal matter, offensive but not pungent, and changes permanently the color of red litmus-paper.

It frequently happens that, on evaporation of the ethereal solution, there remains, in the upper part of the dish, a yellow ring, consisting of the alkaloid in an amorphous, and rather impure condition, but

with the reactions. I consider this treatment with ether a very necessary operation, not only in cases of a volatile, but also in those of a fixed alkaloid. Let us take, by way of illustration, an article of food containing strychnine. Let the substance be treated with strong alcohol, and oxalic or tartaric acid; let the extract be separated from the resi due by filtration, and evaporated; let the resulting aqueous solution be again filtered, to remove fatty and resinous matters, etc., which may have separated; let the filtrate again be evaporated, and the residue be exhausted with cold anhydrous alcohol; let the alcoholic solution be evaporated, and the residue be dissolved in a small quantity of water (the process described § 116–117). Let this solution be divided into two portions. To the first portion, let some bicarbonate, or caustic alkali be added; let the mixture be agitated with ether, and the ethereal solution be evaporated. Let the second portion be agitated with ether as long as this solvent takes up any coloring matter, and the colored ether be removed; let, then, the alkaloid be set free by an alkali, dissolved in ether, and this solution be evaporated. On comparing the two residues, a great difference will be found. The second process yields the alkaloid in a state of greater purity than the first, and almost invariably in a crystallized condition. This is of paramount importance, since it enables us to observe the characteristic reactions with the greatest distinctness. Granted even that ether takes up a trace of the salts of the alkaloid, still the second method deserves the preference, since a small quantity of the alkaloid, in a pure condition, is infinitely more valuable for our purposes than a larger quantity in a state of impurity.

intermixed with some in the pure state, forming more or less distinct crystals. Narcotine occurs in comparatively large crystals; strychnine in small scattered scales; morphine in a similar manner; veratrine pulverulent, or resinous; colchicine resinous. Those particles which appear the purest should be removed with the point of a pen-knife, and preserved for the purpose of being tested with the proper reagents (v. § 122).

§ 121. In order to obtain the largest possible quantity of the alkaloid in a crystallized condition, the residue from the evaporation of the ethereal solutions (§ 120) is dissolved in a few drops of dilute alcohol, and the solution allowed to evaporate. There is usually too much foreign matter present to allow the formation of crystals. The residue must then be treated with water, acidulated with sulphuric acid; the alkaloid is dissolved as a sulphate, and the impurities remain as a greasy coating on the surface of the dish. The limpid solution is poured off, the dish washed with a few drops of acidulated water, and the whole of the liquid placed for a short time in vacuo, or over sulphuric acid, to effect a suitable concentration. To the residue, a very concentrated solution of pure carbonate of potassa is added, and the mixture treated with anhydrous alcohol; the alkaloid enters into solution, and the sulphate of potassa, together with the excess of the carbonate, remains undissolved. The alcoholic solution, on evaporation, yields the alkaloid in crystals, the nature of which has now to be ascertained.

§ 122. It has been remarked before that, in the majority of cases, the analyst will only have to prove

the presence or absence of a certain alkaloid, the nature of which is known from other circumstances. Then, of course, the crystals should first be examined with those reagents which most satisfactorily indicate the presence of this certain alkaloid. It may, however, happen that suspicion does not point to any particular alkaloid, and, in this case, there remains nothing but to make some preliminary tests.* The order to be pursued is of no material consequence. We may, for example, proceed in the following manner:

A particle is placed in a few drops of sulphuric acid, and heat applied: a red color is indicative of veratrine.

A particle is dissolved in cold, concentrated sulphuric acid, and tested for strychnine with a piece of bichromate of potassa.

A particle is placed in a few drops of a solution of iodic acid; a yellow color and odor of iodine points to morphine; on addition of a little starch-paste, the mixture ought to become blue.

A particle is dissolved in water, acidulated with a drop of hydrochloric acid, and a dilute solution of sesquichloride of iron added, by means of a glass-rod; a blue color, more or less pure, betrays also the presence of morphine.

* The examination with those reagents which produce a characteristic color—the color-tests—are best performed in small porcelain dishes, since the colors appear on a white surface most distinctly, and in greatest purity. Those tests which consist in the production of colorless or but little colored precipitates, are best performed in watch-crystals, placed on a dark-colored support; slight precipitates are thus easily perceived.

A particle is mixed with a few drops of concentrated nitric acid: a violet color indicates colchicine.

A particle is dissolved in water, containing a little caustic soda, and tested with blue vitriol for picrotoxine (v. § 115).

If the nature of the alkaloid has thus been determined, the remaining portion of the residue is used for making the other reactions. It may, for instance, be dissolved in water, slightly acidulated with sulphuric, or hydrochloric acid, and the solution be tested with tannine, terchloride of gold, bichloride of platinum, sulphocyanide of potassium, etc.

[Another mode to distinguish the different fixed alkaloids of which the residue in question might consist, is that proposed by Schneider.*

A portion of the residue is neutralized with dilute hydrochloric acid, and thus a concentrated aqueous solution prepared. To this liquid, a solution of caustic potassa is very gradually added. If a precipitate is formed, the reagent is added in excess, to ascertain whether an excess of the alkali dissolves the precipitate, or not. If the precipitate disappears, the alkaloid is either *morphine* or *colchicine*. They are easily distinguished by the reactions given in § 106 and § 113.

If the precipitate did not dissolve in an excess of the reagent, it is collected on a filter, washed with a little water, and then dissolved in dilute sulphuric acid. The acid liquid is mixed with a solution of bicarbonate of soda (saturated in the cold), until the acid reaction has just disappeared, well agitated, and

* Die gerichtliche Chemie, von Dr. F. C. Schneider. Wien. 1852.

left to rest for some time. The formation of a precipitate points to *narcotine*.

If no precipitate was produced by bicarbonate of soda, a fresh portion of the residue under examination is digested with anhydrous alcohol in a test-tube closed with a cork-stopper. If the substance remains undissolved, it is *strychnine* (to be corroborated by the reactions given in § 108); if it dissolves, it may be *veratrine* or *brucine*. The latter two are distinguished by their behavior towards nitric acid (v. § 109 and § 112)].

§ 123. M. Stas, in pursuing the course above described, has succeeded in isolating from mixtures with foreign substances, the following alkaloids: morphine, codeine, strychnine, brucine, veratrine, emetine, colchicine, aconitine, atropine, and hyoscyamine. Thus, he has extracted morphine from opium; strychnine and brucine from *nux vomica;* veratrine from extract of veratrum; emetine from extract of ipecacuanha; colchicine from tincture of colchicum; aconitine from the aqueous extract of aconite; hyoscyamine from a very old extract of hyoscyamus. Of the volatile alkaloids, he thinks that conicine, nicotine, aniline, picoline, and petinine, may be detected. In cases where the exact nature of the alkaloid escapes detection, M. Stas considers it very probable that at least the natural family of plants in which it occurs may be ascertained.

§ 124. Numerous experiments, made in my laboratory, have proved the method of Stas to be very exact for the detection of the volatile alkaloids, and also for strychnine and veratrine. But to show the

presence of morphine, some precautions must be used, lest it should escape detection.

Mr. Von Poellnitz has proved, experimentally, that, when the solution of a salt of morphine is mixed with carbonate of soda, and agitated with ether immediately afterwards, the ether dissolves the alkaloid, and deposits it in crystals on evaporation. But, when the ether is added after some time only, the morphine separates in a crystalline condition, and on then agitating the mass with ether, this solvent does not take up any appreciable quantity. It is, therefore, absolutely necessary that the ether be added immediately after neutralization of the aqueous solution of the salt of morphine with bicarbonate of soda has been effected (v. § 117); the ethereal solution should be poured off as soon as possible and then exposed to evaporation. Professor Polstorff states that ether containing some alcohol is a better solvent for morphine than pure ether.

On account of the easy solubility of morphine in alkaline liquids, it is of importance that the alkaline solution (§ 117), after having been repeatedly agitated with ether, should not be thrown away, but subjected to a further treatment. The ether is removed by gentle heat; if the liquid appears turbid from particles of morphine, a little caustic soda is added; the limpid liquid is then mixed with a strong solution of chloride of ammonium, and exposed to the atmosphere in an open vessel. If any morphine is present, it will separate in crystals.

§ 125. M. Stas, in his memoir, expresses himself strongly against the use of the tribasic acetate of lead, and that of charcoal, as purifying and decolor-

izing agents. He urges against the use of the lead-salt, that it does not completely remove all foreign matter; that the sulphureted hydrogen, which has to be passed through the liquid to precipitate the excess of lead, enters into combination with many organic substances, forming compounds of a very unstable character, which undergo decomposition on exposure to air, or on application of heat, and thereby cause the liquid to assume a more or less dark color, and disagreeable odor, an odor which remains tenaciously adhering to the substances afterwards extracted from these liquids; that a poisonous substance is brought into the matters, and that thus the opportunity is lost of subsequently examining them for mineral poisons. The use of animal charcoal for the purpose of decolorizing is inadmissible, on account of its property of removing alkaloids from solutions; the whole of the poison may thus be lost.

§ 126. This property of animal charcoal has been taken advantage of by Graham and Hofmann,* to detect the presence of strychnine in beer. It is evident that the same method is equally well adapted for other liquids and a great many other alkaloids. These gentlemen proceeded in the following manner:

The suspected beer is left for twelve hours in contact with animal charcoal, with frequent stirring. The liquid is then separated from the charcoal by filtration, and the latter washed once or twice with a little water. The charcoal has taken up all the strychnine, and the filtrate is free from any bitter

* Annalen der Chemie und Pharm. Bd. 83. p. 39, also Pharm. Journal and Transact. Vol. xi. p. 504–506.

taste. In order to obtain the alkaloid from the charcoal, the latter is treated with boiling alcohol for half an hour. From the alcoholic extract, the alcohol is removed by distillation; to the remaining aqueous liquid, some caustic soda is added, until it shows an alkaline reaction; the mixture is agitated with ether, and the ethereal solution exposed to evaporation. The residue is tested with sulphuric acid and bichromate of potassa, or ferrocyanide of potassium.

[MM. Graham and Hofmann satisfied themselves, by a series of experiments, of the exactness of their method. Half a grain of strychnine was dissolved in half a gallon of beer; two ounces of animal charcoal were then added, and left in contact with the liquid for twenty-four hours. The charcoal was then separated from the liquid by filtration, and boiled for half an hour with eight ounces of alcohol, care being taken to replace, by fresh portions of alcohol, the loss caused by vaporization. The alcohol was then removed by distillation, the residue mixed with caustic potassa, agitated with ether, and the ethereal solution exposed to spontaneous evaporation on a watch-crystal. On addition of a drop of sulphuric acid and a particle of bichromate of potassa, the characteristic violet color was produced.]

§ 127. In a case of poisoning with tincture of colchicum, which occurred in Berlin (Pharm. Centralblatt. 1855. p. 139), MM. Schacht and Casper extracted the alkaloid [colchicine?] in following essentially the method of Stas.

Wittstock treated the contents of the stomach with alcohol, mixed with a few drops of hydrochloric acid;

concentrated the liquid by evaporation at 30° C., to the consistency of a thin syrup; treated the residue with water; separated the liquid by filtration from the insoluble fatty matter; and brought the liquid again to the consistency of a syrup. The residue he dissolved in water; added *magnesia usta*, in order to set the alkaloid free, agitated the mixture with ether, and exposed the ethereal solution to evaporation. The residue from the last operation possessed a bitter taste, and its solution in acidulous water gave a white precipitate with tannine, a yellow precipitate with bichloride of platinum, and a kermes-brown precipitate with tincture of iodine. By a similar process he extracted the alkaloid from the tincture of colchicum.

§ 128. If it is the object of the investigation simply to show the presence of a volatile alkaloid, the method of Stas may be slightly modified. The substances are treated with alcohol and tartaric, or oxalic acid; the extract is concentrated by evaporation; the resulting aqueous solution is separated by filtration from the insoluble matters; the filtrate is mixed with a solution of caustic soda, and distilled. The alkaloid will be found in the distillate. For its separation, two ways may be followed. The distillate is either agitated with ether, and the ethereal solution exposed to evaporation; or it is neutralized with oxalic acid, the liquid concentrated by evaporation, and the residue treated with caustic soda and ether, when also an ethereal solution of the alkaloid is obtained. Operating in this manner, Lehmann (Pharm. Centralblatt. 1853. p. 927) detected nicotine in the stomach of a boy who died of the effects

of an infusion of tobacco-leaves, and, in my laboratory, it has repeatedly been extracted from a cigar.

§ 129. If the presence of opium has to be established, the operations may be so conducted that the resulting solution contains a salt of meconic acid; the latter is then easily detected by its reaction with sesquichloride of iron. The substances are treated with dilute alcohol and a few drops of hydrochloric acid; the extract is concentrated by evaporation; the residue dissolved in water; the aqueous liquid separated by filtration from insoluble matters; the filtrate mixed with *magnesia usta* in excess, and heated to ebullition; then filtered. The resulting liquid contains meconate of magnesia. It is acidulated with hydrochloric acid, and mixed with a few drops of sesquichloride of iron. In presence of meconic acid, the liquid assumes a dark, brownish-red color. Since opium is the only substance in which meconic acid occurs, to have proved the presence of this acid is to have proved the presence of opium.

[Though the detection of meconic acid is undoubtedly a conclusive proof for the presence of opium, still Stas' method, by which the morphine is obtained, deserves, in my opinion, the preference, and for this simple reason, that some kinds of opium, according to Robiquet, *do not contain the slightest trace of meconic acid.* It might, therefore, happen that, notwithstanding large quantities of opium have been administered, the analyst might fail to detect its presence.

In regard to the blood-red color which meconic acid produces in solutions of the sesquisalts of iron, it must be remembered that sulphocyanides and ace-

tates give a very similar reaction. In the case of an acetate, the color is destroyed on addition of dilute acids, and, on boiling, a brownish-red precipitate is thrown down. In the case of meconic acid, or a sulphocyanide, the color does not disappear on addition of dilute acids, not even on boiling. Terchloride of gold destroys the color produced by a sulphocyanide, but not that produced by meconic acid.—(*Vogel.*)

To obtain additional proof as to the nature of the acid, the filtrate containing the meconate of magnesia may be precipitated with nitrate of silver. White meconate of silver is thrown down, which is collected on a filter, and washed with water. During this operation, it is frequently converted into white lustrous crystalline scales. It dissolves completely in moderately strong nitric acid; on applying heat to the solution, violent effervescence takes place, cyanide of silver is precipitated, and the liquid contains oxalate of silver.]

APPENDIX.

GENERAL METHOD.

§ 130. It has been repeatedly remarked in the preceding pages that, before proceeding with a chemico-legal investigation, circumstantial evidence has usually thrown some light on the matter, and pointed out the nature of the poison. It may, however, happen that no such indications have been previously gathered, and the question arises: "How shall we operate under these circumstances?" From what has been said in regard to the detection of the individual poisons, or groups of poisons, a general method may be deduced, which leads to the detection of any poison, and which does not even require a division of the material under examination.

The substances under examination, if not possessing an acid reaction, are slightly acidulated, and placed in a retort provided with a receiver. A few pieces of sulphur are added, and the retort heated over a water-bath until a few grammes have passed over. The distillate is tested for hydrocyanic acid (§ 75). If no hydrocyanic acid is found, the heat may be slightly increased in order to cause the phosphorus, which might be present. to combine with the sul-

phur, and to produce the characteristic light. Both the distillate and the pieces of sulphur are afterwards examined for phosphorus (v. § 96). If no phosphorus is found, the contents of the retort are examined for the presence of alkaloids, after the method of Stas (v. § 116, etc.) As in this process no poisonous substances of any kind are introduced into the mass, it may finally be examined for mineral poisons, if no alkaloid should have been detected. For this purpose, all the different residues, extracts, and liquids, are united; ether and alcohol are removed by evaporation, and the remaining mass treated as described § 59, etc.

CHAPTER VIII.

ON THE EXAMINATION OF BLOOD-STAINS.

§ 131. IT is sometimes of great importance to identify spots of blood on clothes, on the soil, furniture, or on the instrument with which death has been inflicted. Though the identification is very easy in some cases, in others again, it is attended with considerable difficulties, and a satisfactory result only to be arrived at with the greatest care and circumspection. This will be readily conceived if we recall to our minds the great variety of circumstances under which an examination of this kind may be asked for. The stains may be on white or colored clothes; they may be on cotton or linen fabrics, on fibres free from nitrogen, or they may occur on silk or wool, on fibres containing nitrogen; they may be recent, or they may be old; they may be unaltered, or they may have been partially removed by washing with water; the soiled instrument may be of iron or steel, or any other metal, it may have been bright or rusty, etc., and all these different circumstances will, of necessity, influence to some degree the *modus operandi.*

We shall confine our remarks to the chemical ex-

amination; the microscopical test, which, in many cases, is undoubtedly of great value, we shall leave to those who are sufficiently qualified to escape its fallacies. The former mode of testing admits of more extended application than the latter, since we can detect the constituents of the blood by chemical reactions, in cases where the microscopical test fails to discover even the slightest trace.

§ 132. We shall first consider the case where the spots are on undyed cloth, linen, or cotton. The stains appear of a more or less dark, red-brown, or black-brown color, and impart to the cloth a kind of stiffness. A spot is cut out, and suspended in a small quantity of distilled water; it softens, reddish-brown stripes are produced in the water, and the stains disappear from the cloth more or less completely.

The liquid thus obtained, which is of a reddish-yellow, or brown color, is heated in a test-tube. If the stain consisted of blood, the liquid looses color, becomes opalescent, and sometimes greyish-white, flakes of coagulated albumen are observed to separate. If, then, a solution of nitrate and nitrite of mercury* is added, and heat applied, the flakes assume a brick-red, or brownish-red color of more or less purity. The same reaction is obtained on adding the mercury solution directly to the liquid under examination, and applying heat.

On addition of nitric acid to the liquid, whitish flakes separate; on heating, they assume a more or less pure yellow color.

* This solution, the best reagent for proteinaceous bodies, is prepared by dissolving mercury in an equal weight of red, fuming nitric acid, and adding to the liquid twice its volume of water.

Chlorine-water produces white flakes, especially on heating.

A solution of tannine gives a whitish precipitate.

On adding to the liquid a few drops of acetic acid, and subsequently a drop of ferrocyanide of potassium, a white precipitate, or turbidness is produced.

The flakes of coagulated albumen, which formed on heating the liquid, dissolve on addition of a few drops of caustic soda; they are re-precipitated from this solution on addition of nitric acid, or chlorine-water.

On evaporating the liquid in a porcelain dish, a brown, lustrous coating remains; on pouring chlorine-water on it, and again evaporating, a colorless residue is obtained, which, on addition of a little water and sulphocyanide of potassium, assumes a reddish color (owing to the iron of the blood).

§ 133. If the liquid (the solution of the stain in water) is mixed with some pure carbonate of potassa, the mass evaporated, the residue heated to dryness at 100° C.; then placed in a long and narrow glass-tube, covered with some dry carbonate of potassa, and strongly and continuously heated by means of the blow-pipe, a mass is obtained which contains cyanide of potassium. When the tube has cooled, it is cut off above the fused mass, and the latter, together with the lower end of the tube, thrown into a test-tube; some water and a few particles of iron filings, or better, sulphuret of iron, are added, and gently heated. Ferrocyanide of potassium is formed. The liquid is filtered, the filtrate slightly acidulated with hydrochloric acid, and mixed with a few drops of sesquichloride of iron; the liquid assumes a

greenish, or bluish color, and deposits, after a while, a precipitate of Prussian blue (*Löwe*, Pharm. Centralblatt. 1854. p. 137).

In order to obtain this characteristic reaction, we may also treat the spots with alkaline water, add carbonate of potassa to the extract, then evaporate, etc.

Or the cloth containing the spots is calcined in a porcelain capsule until it is easily rubbed to powder, and mixed with carbonate of potassa; this mixture is then strongly ignited, and otherwise treated, as before.—(*Wiehr*, Pharm. Centralblatt. 1854. p. 431).

It is evident that these experiments require the absence of all other nitrogenized bodies; and it should, therefore, not be neglected to submit a piece of the unstained cloth to exactly the same treatment.

§ 134. If an attempt has been previously made to remove the stains by means of boiling water, nothing will be dissolved by a subsequent treatment with water, because the albumen has become coagulated. In this case, water is used, which contains some caustic potassa; the resulting solution gives white precipitates with nitric acid, hydrochloric acid, and chlorine water, and the presence of a proteinaceous substance may be shown by the treatment described in § 133.

The stains, by being treated with alkaline water, do not lose their color. If then exposed to the action of hydrochloric acid, the coloring matter is dissolved; on evaporating the solution to dryness, a residue is obtained which becomes blue with ferrocyanide of potassium, and red with sulphocyanide of potassium.—(*M. Morin*, *faits pour servir à l'his-*

toire du sang, considéré sous le rapport de la chimie légale, private communication.)

§ 135. If the stains are on dyed, or printed linen, or cotton clothes, the spots are cut out, and macerated with water, as in the preceding case. If the colors are fast, the same kind of solution is obtained; but, if they are wholly, or partially soluble in water, the coloring matter of the blood becomes mixed with the dyes, and the reactions which this solution gives with the proper reagents will not be so distinct, or so conclusive for the presence of blood as in the case of undyed stuffs. In this case, the formation of cyanide of potassium is the principal reaction; the process is the same as that described § 133. It is necessary that an unstained piece of the cloth be subjected to the same treatment, and only if here no similar reaction is observed, we can rest satisfied that the cyanide was not produced from the constituents of the dye. The same remark applies to the case where the stains have been macerated in alkaline water.

§ 136. Stains on woollen stuffs are first macerated in water, in order to obtain a solution which may be tested with the proper reagents. It must be borne in mind that woollen fibre contains nitrogen, and that it gives rise in itself to the formation of cyanide of potassium when treated as described § 133. Hence, before evaporating the liquid and fusing the residue with carbonate of potassa, care must be taken to remove any particles of fibre which might be present. If a treatment of the stuff with alkaline water becomes necessary, but very little caustic potassa should be added, or, what is preferable, ammonia should be used instead of potassa. The reason for

this is, that woollen fibre is soluble in potassa, but is not affected by ammonia. During the subsequent evaporation of the liquid, the ammonia passes off. It is absolutely necessary that an unstained piece of the cloth be treated in the same manner, for reasons above stated.

§ 137. Spots on wood, or stone, are carefully scraped off with a chisel, or a knife, then macerated in water, or alkaline water, and treated in the man- above described. Soil, impregnated with blood, is macerated in pure water, or in water containing potassa, or ammonia (*Lassaigne*, Pharm. Central-blatt. 1850. p. 365). Stains on iron are scraped off, and a small portion of it heated in a glass-tube, in order to produce the peculiar odor which is evolved on carbonizing animal matter; the residue may then be fused with carbonate of potassa. Another portion of the scraped off mass is macerated in water, or alkaline water. It is well known that iron-rust always contains some ammonia; hence, it becomes necessary to dry the mass thoroughly, in order to expel the ammonia, before fusing it with carbonate of potassa.

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